Eurokin, 20th Anniversary Symposium, October 16-17, 2018, Vaalsbroek

First Principles Multiscale Modelling to design Pt-based bimetallic catalysts for (de)hydrogenation reactions

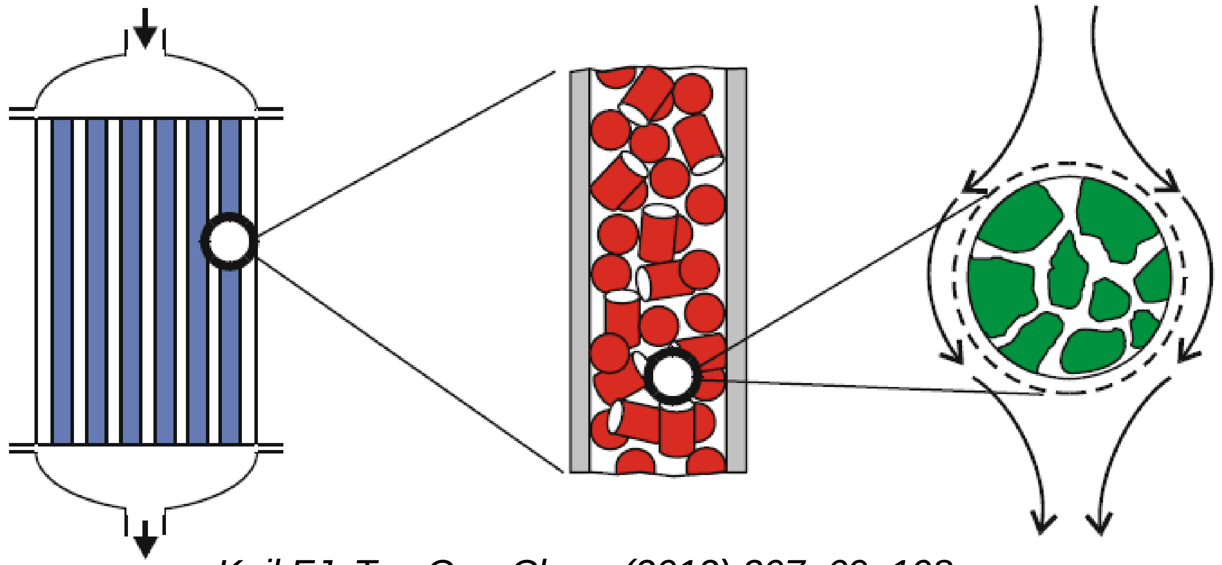
Marie-Françoise Reyniers, Maarten K. Sabbe and Guy B. Marin

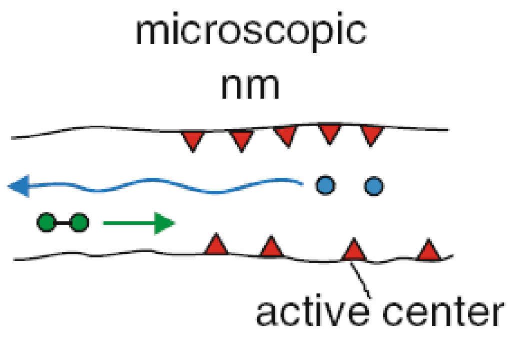
Laboratory for Chemical Technology

GHENT UNIVERSITY

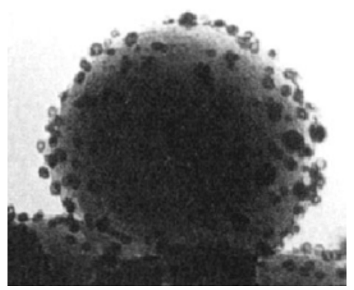
LCT DRIVING CHEMICAL TECHNOLOGY

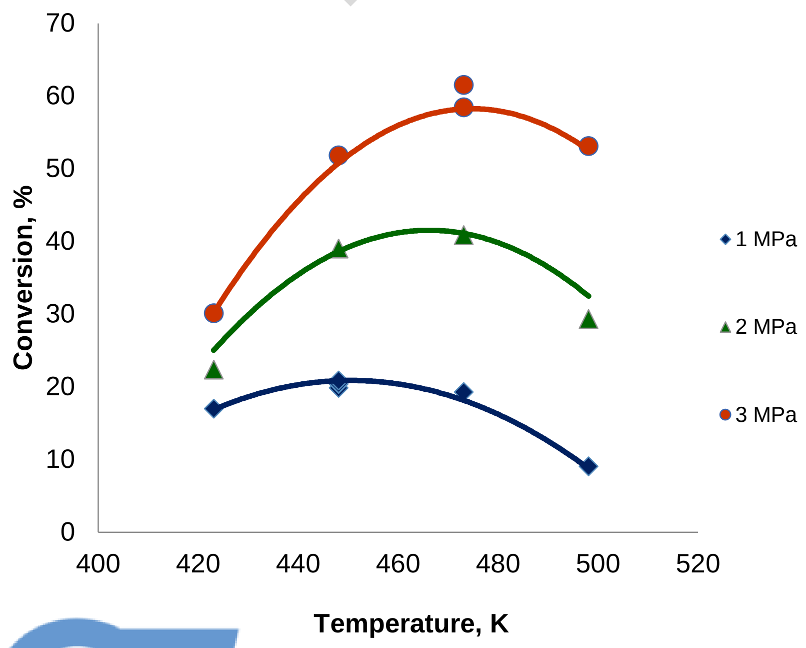
Metal catalyzed processes



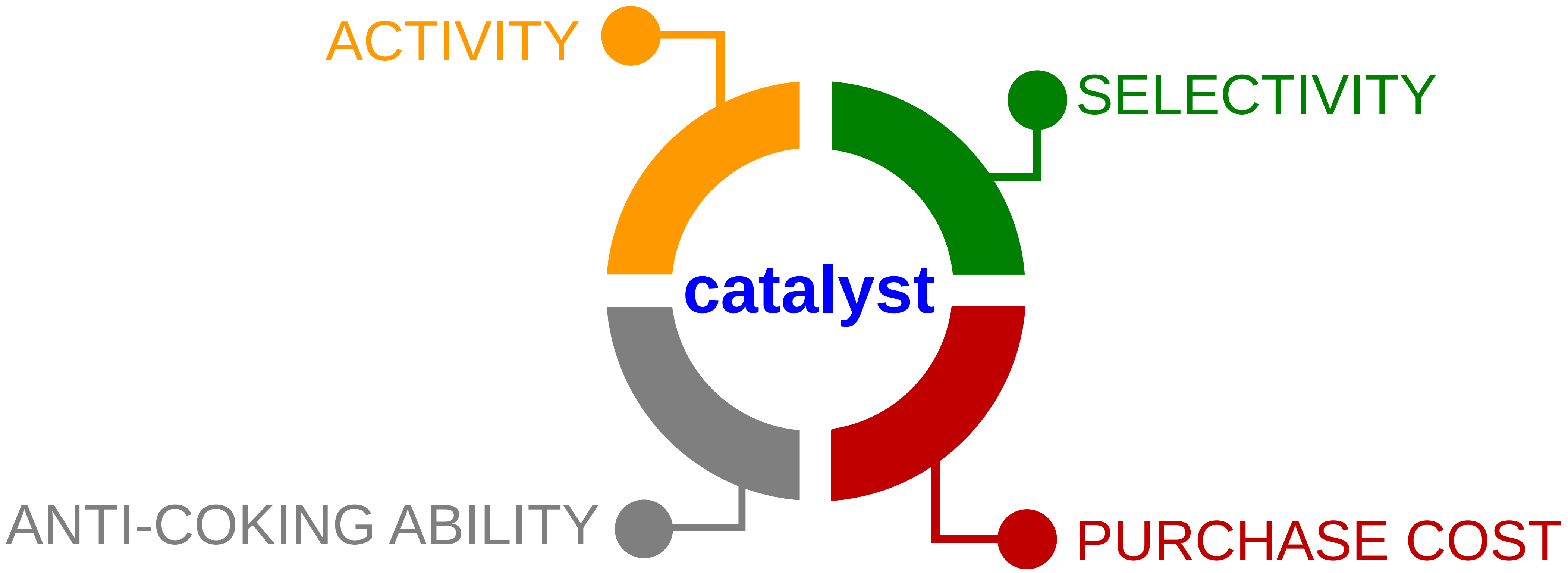


Keil FJ, Top Curr Chem (2012) 307: 69–108





Metal catalyst design: goal



ACTIVITY

SELECTIVITY

catalyst

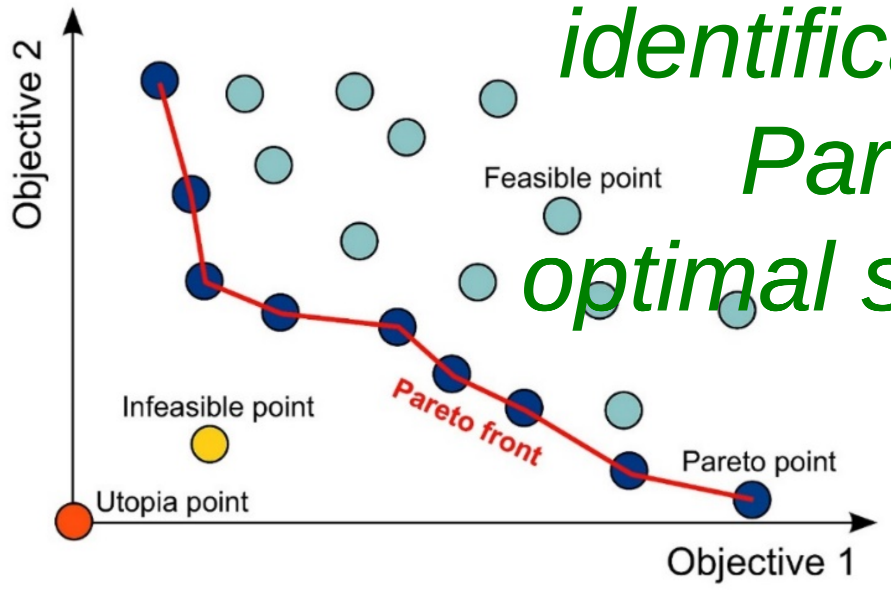
ANTI-COKING ABILITY

PURCHASE COST

Find best trade-offs by optimizing:

- catalyst composition
- reaction conditions:
  - pressure
  - temperature

Conflicting objectives



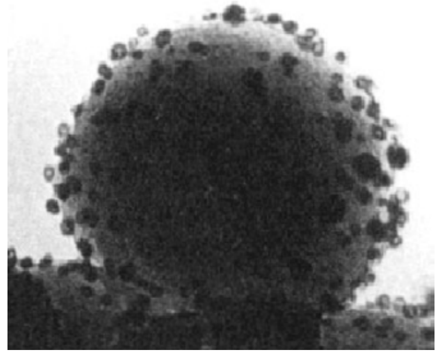
identification of Pareto optimal solutions

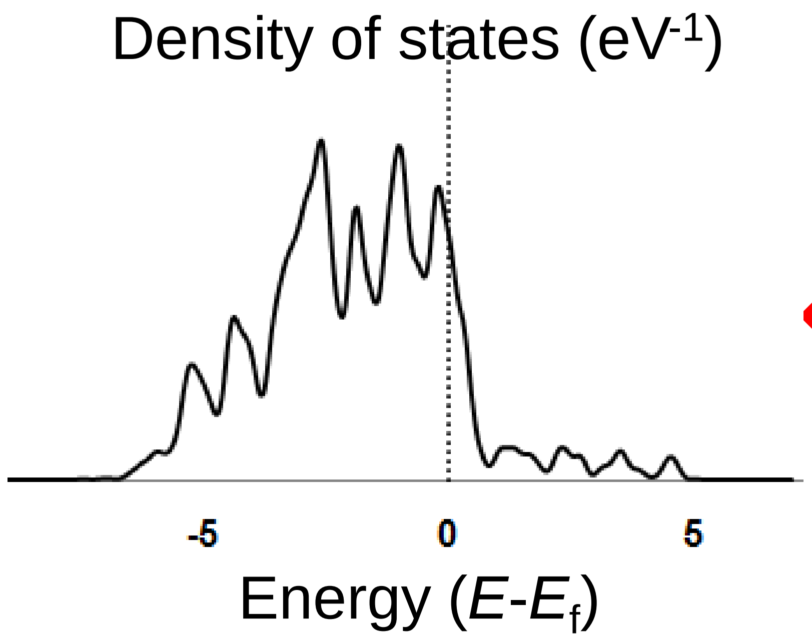
GHENT UNIVERSITY

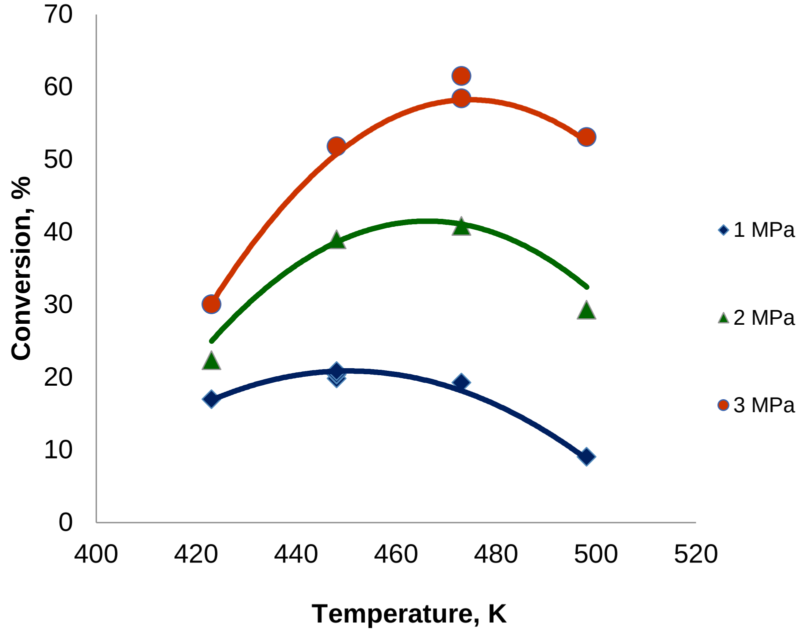
DRIVING CHEMICAL TECHNOLOGY

Metal catalyst design: approach

catalyst composition & structure → electronic structure → reactivity & selectivity





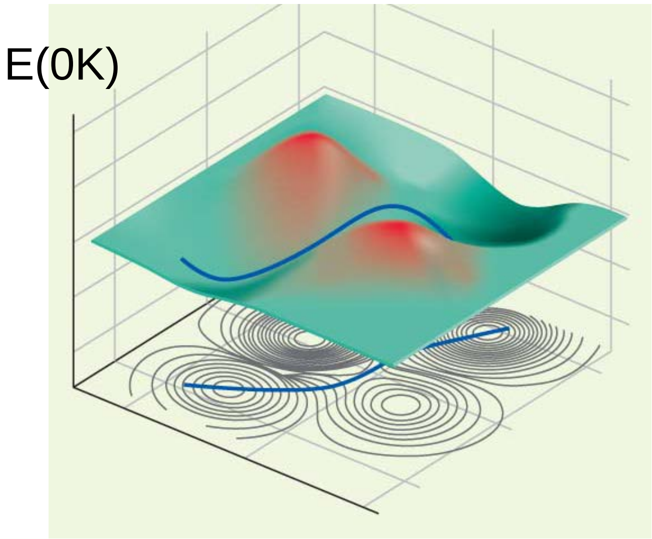


First principles based multiscale modelling of catalytic processes

electronic structure
(0 K)

vibrational analysis

statistical
thermodynamics



H(T), S(T), G(T)

thermo & kinetics
K, k_+, k_-

= ***f(catalyst descriptor)***

reactor hydrodynamics
mass/heat transport

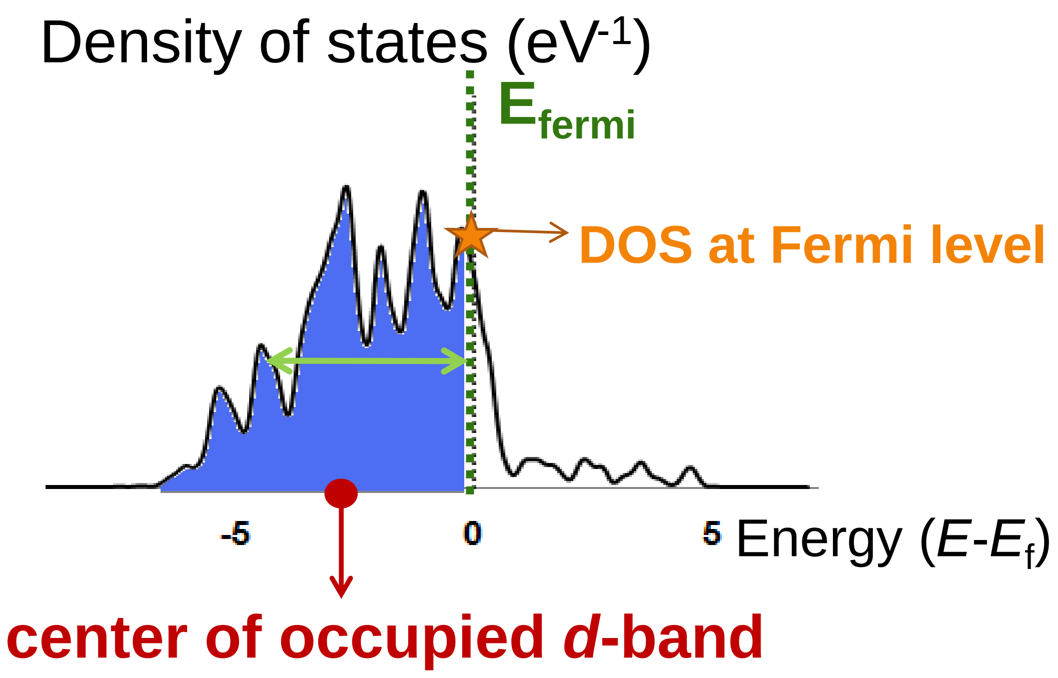
- surface coverages
- rate analysis
- operative mechanism
- conversion & product yields

guidlines for optimal catalyst properties & reaction conditions

GHENT UNIVERSITY

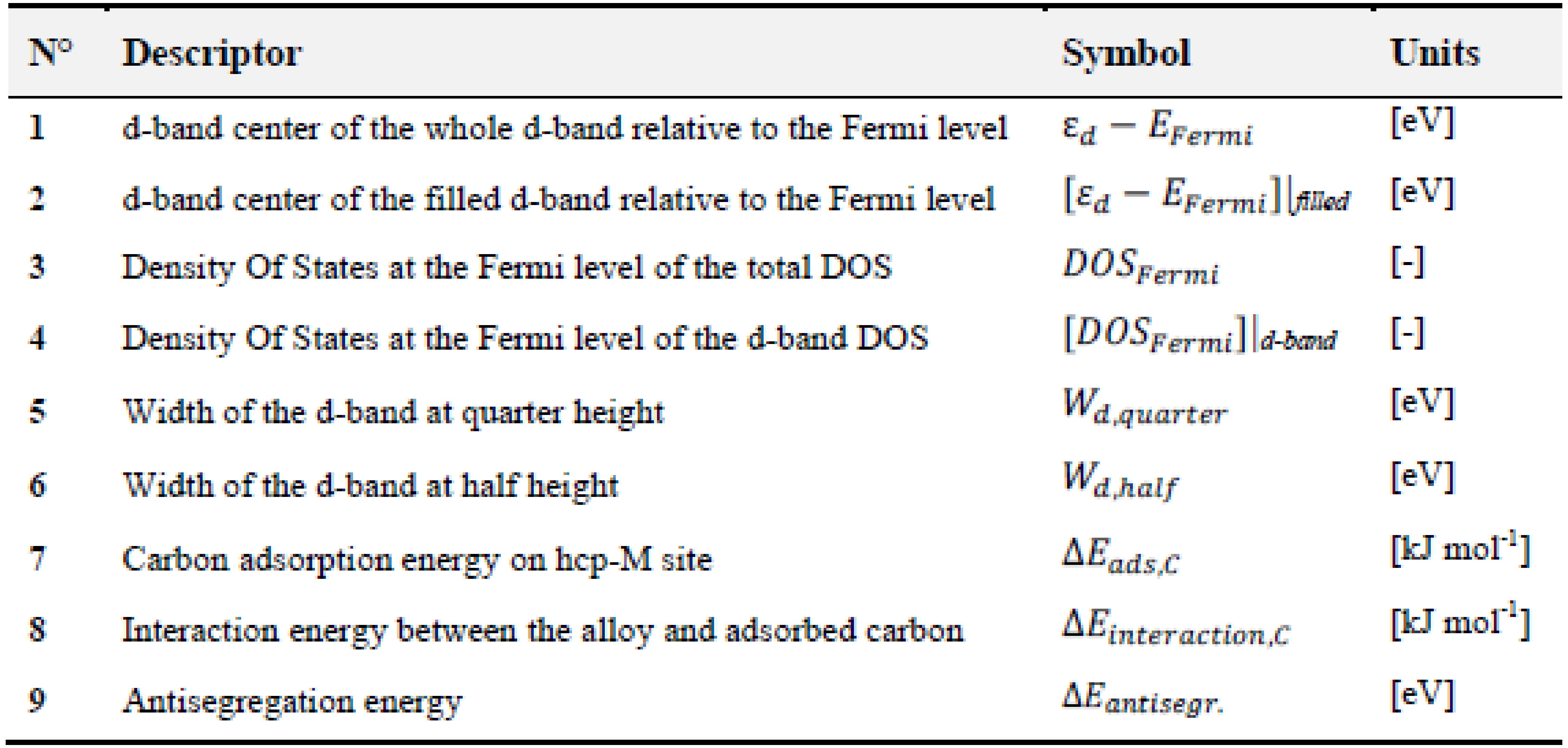
LCT
DRIVING CHEMICAL TECHNOLOGY

Use d-band property as catalyst descriptor



DOS at Fermi level

center of occupied *d*-band

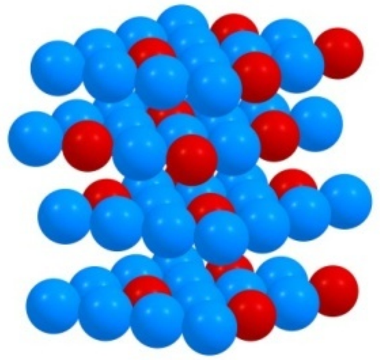


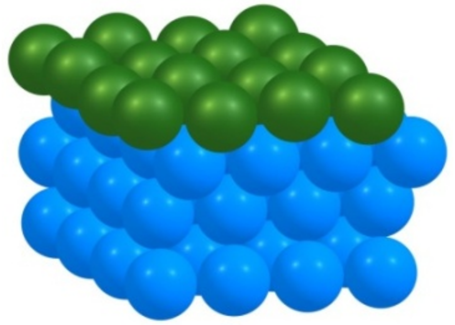
N°	Descriptor	Symbol	Units
1	d-band center of the whole d-band relative to the Fermi level	$\varepsilon_d - E_{Fermi}$	[eV]
2	d-band center of the filled d-band relative to the Fermi level	$[\varepsilon_d - E_{Fermi}]\|_{filled}$	[eV]
3	Density Of States at the Fermi level of the total DOS	DOS_{Fermi}	[-]
4	Density Of States at the Fermi level of the d-band DOS	$[DOS_{Fermi}]\|_{d\text{-}band}$	[-]
5	Width of the d-band at quarter height	$W_{d,quarter}$	[eV]
6	Width of the d-band at half height	$W_{d,half}$	[eV]
7	Carbon adsorption energy on hcp-M site	$\Delta E_{ads,C}$	[kJ mol^{-1}]
8	Interaction energy between the alloy and adsorbed carbon	$\Delta E_{interaction,C}$	[kJ mol^{-1}]
9	Antisegregation energy	$\Delta E_{antisegr.}$	[eV]

Catalyst descriptor: principle

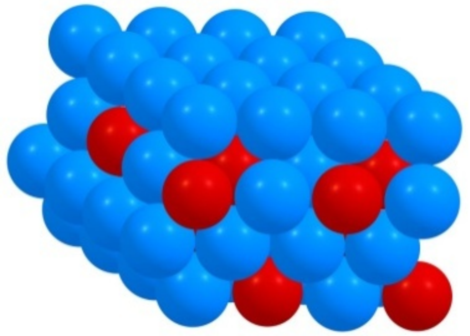
Pt_3M alloys (111); M = Ag, Au, Cu, Fe, Co, Ni, Pd

Pt_3M bulk alloy



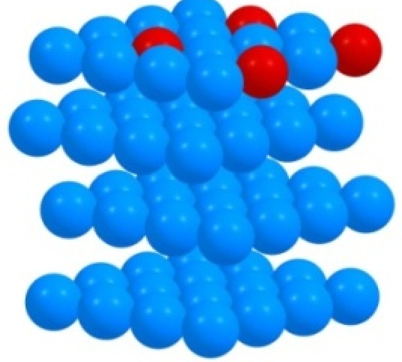


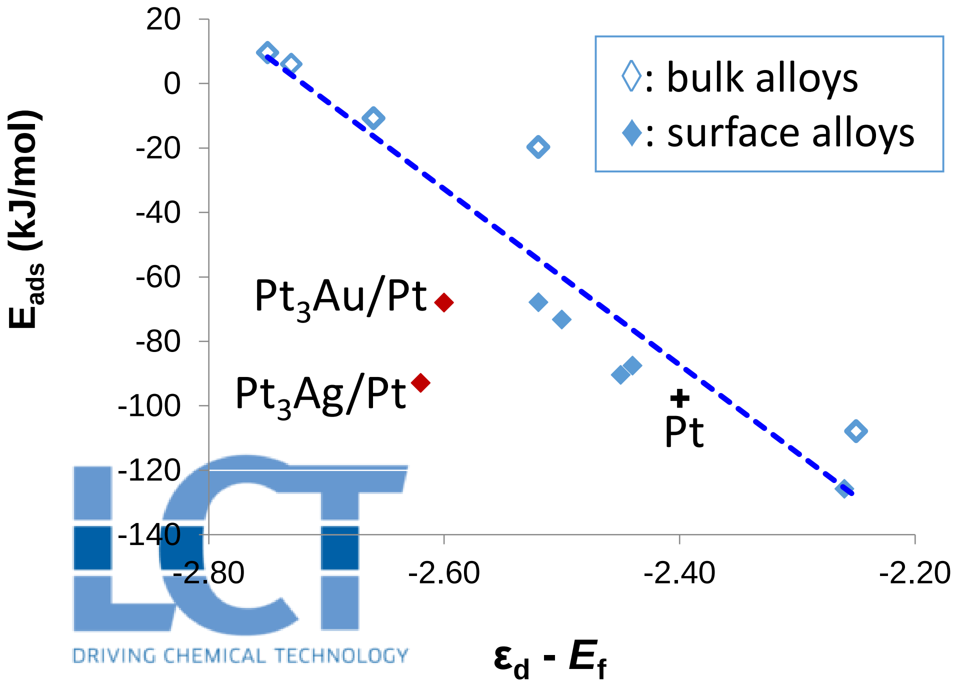
segregated

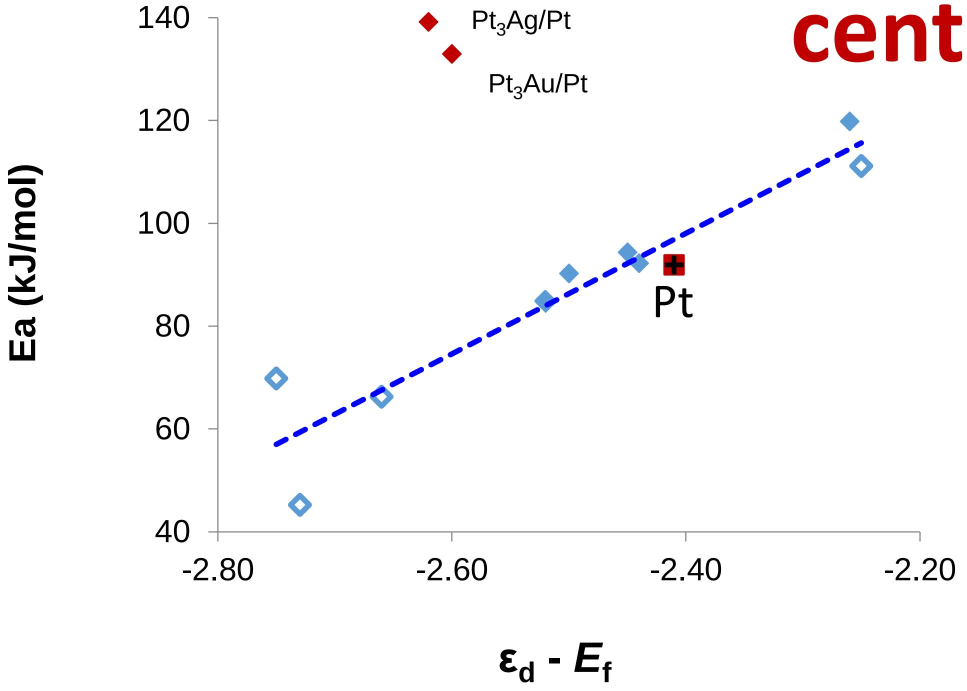


anti-segregated

Pt_3M/Pt surface alloy







center occupied *d*-band

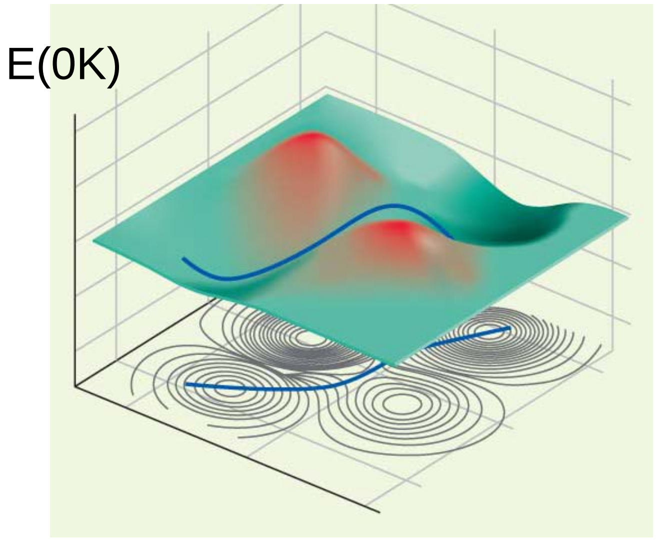
- most stable alloy
- most stable benzene adsorption site
- E_a first H-addition

Challenges FP-modeling catalytic reactions

electronic structure
(0 K)

vibrational analysis

statistical
thermodynamics

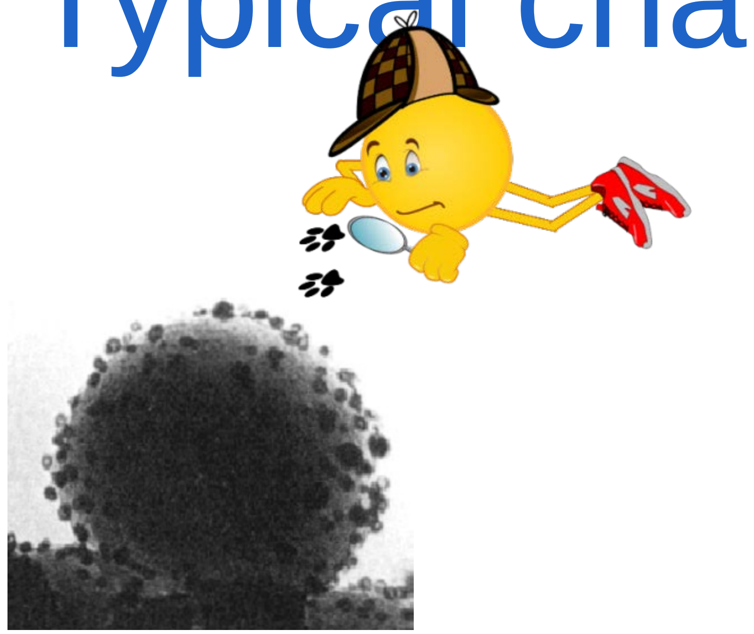


H(T), S(T), G(T)

thermo & kinetics
K, k_+, k_-

introduction | approach | challenges | case benzene | case propane | take home

Typical challenges: 1.the “active site”

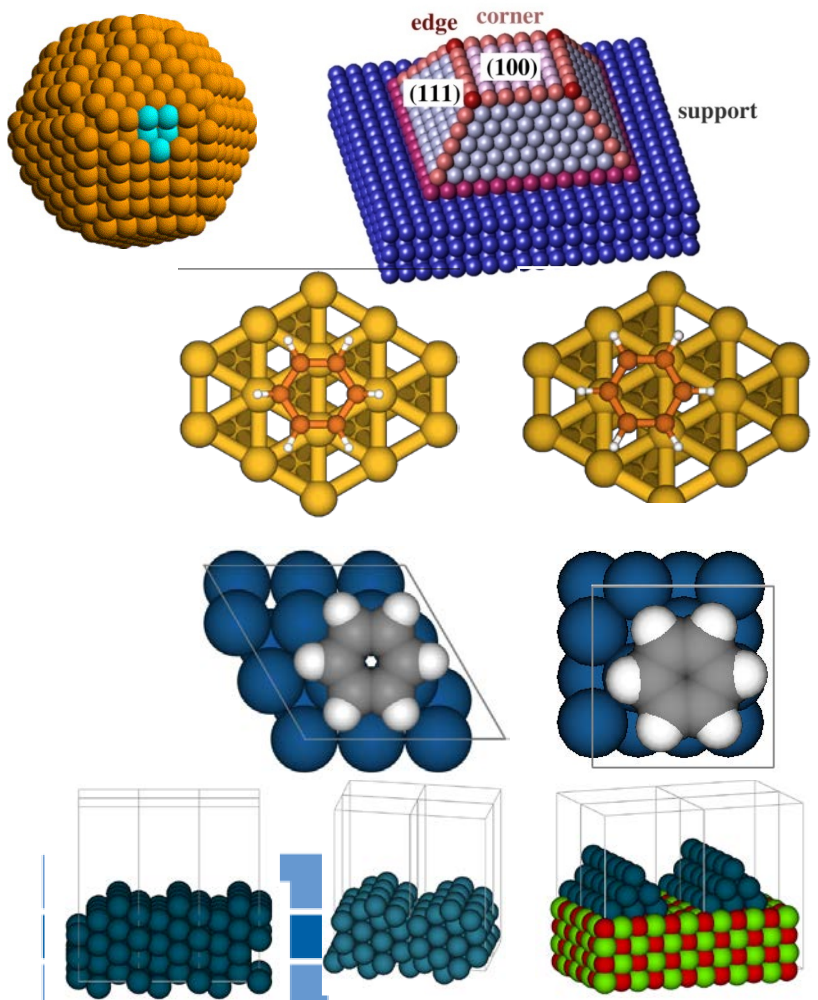


- The “active site” as defined in *IUPAC Gold Book*

“*The term is often applied to those sites for adsorption which are the effective sites for a particular heterogeneous catalytic reaction*.”

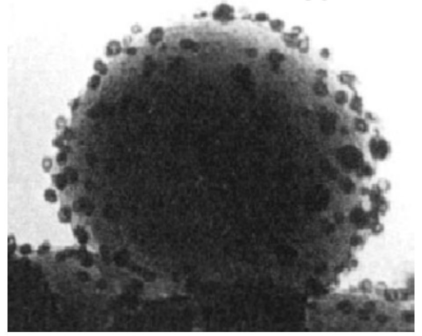
- The “active site” as frequently used in kinetic modeling
  - a single type of site
  - uniformly distributed over the surface
  - represented by ★

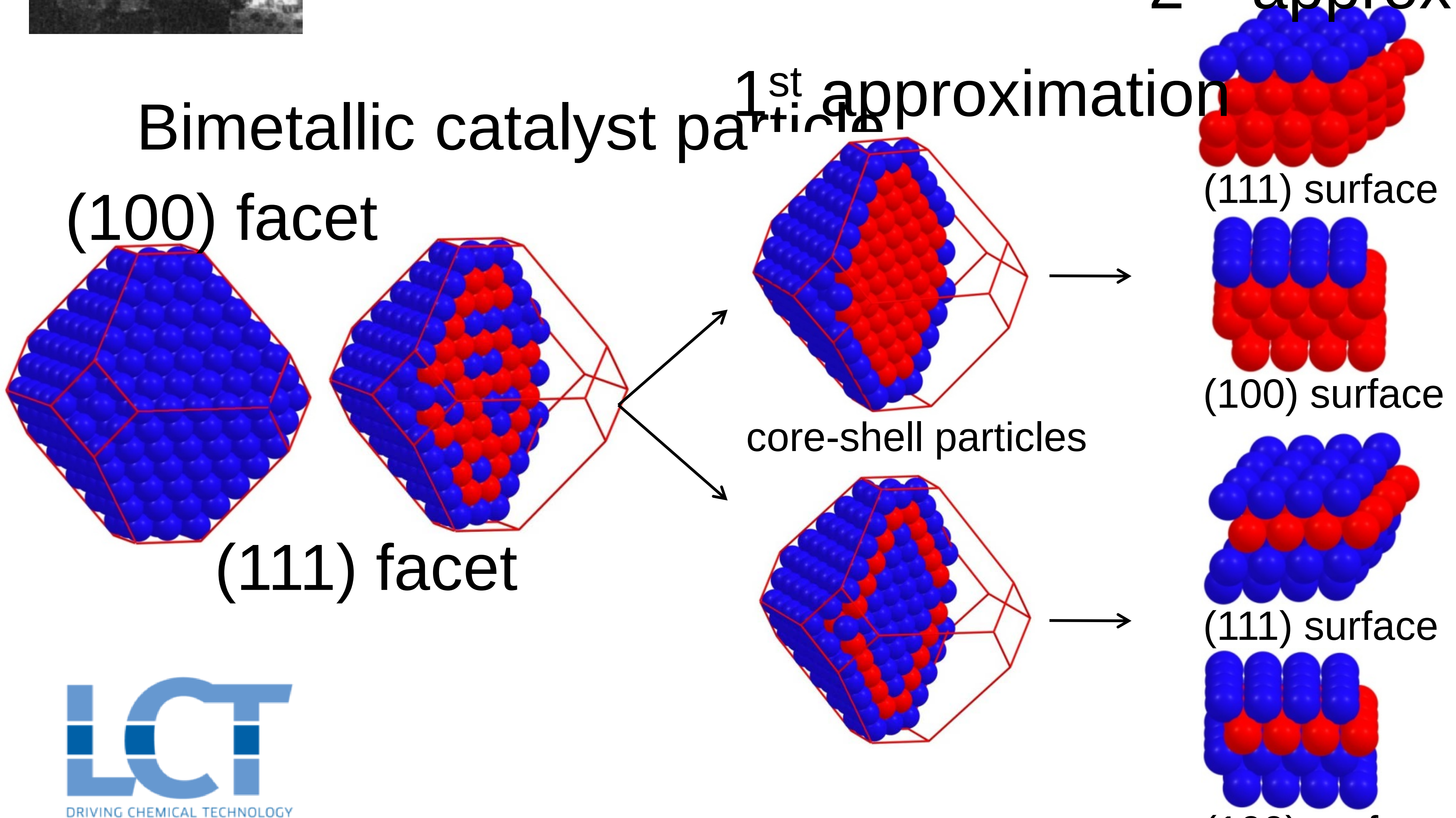
- The “active site” as required for first principles calculations
  - a precisely formulated, atom-defined entity:
    - well-defined surface structure
    - well-defined site geometry (xyz coordinates)
    - multiple catalyst-adsorbate bonding patterns
    - precise amounts of dopants, additives, adatoms
    - particular edge and support effects



Molina and Hammer,
Phys. Rev. Lett., 2003, 90:206102.

Bimetallics: the “active site”





Bimetallic catalyst particle

(100) facet

(111) facet

1^{st} approximation

core-shell particles

2^{nd} approximation

(111) surface

(100) surface

‘skin’ or
‘monolayer’
models

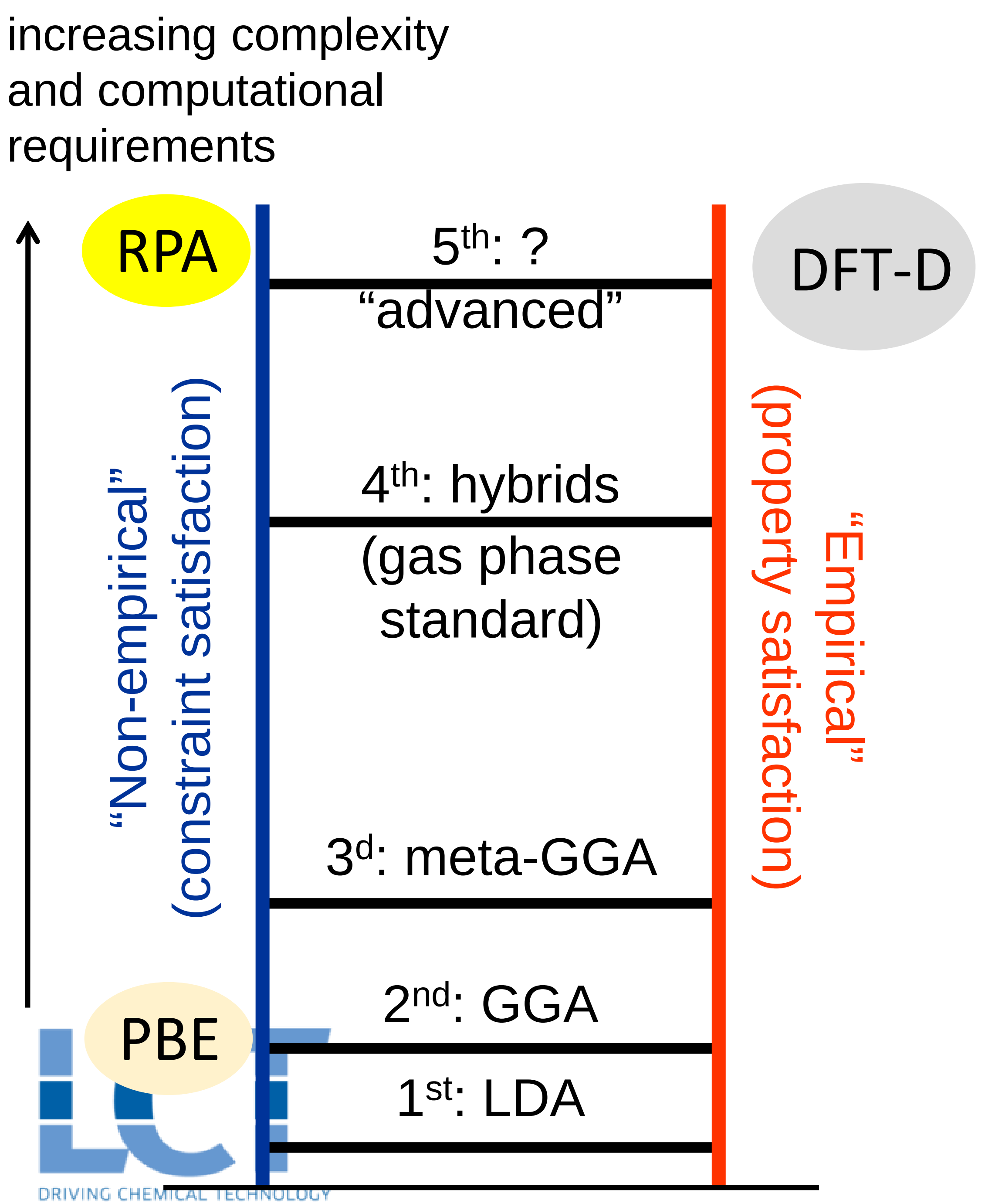
(111) surface

(100) surface

‘surface sandwich’
models

Typical challenges: 2. computational method

Jacob's ladder illustrates DFT functional hierarchy



increasing complexity and computational requirements

RPA

DFT-D

5th: ? "advanced"

4th: hybrids (gas phase standard)

3d: meta-GGA

2nd: GGA

1st: LDA

PBE

"Non-empirical" (constraint satisfaction)

"Empirical" (property satisfaction)

PBE is the common workhorse for heterogeneous catalysis

- no van der Waals interactions
- generic uncertainty of 20-30 kJ/mol through error cancellation

'semi-empirical' DFT- D methods

- fast: negligible computational cost
- parameterized ⇒ manifold of methods
- performs well for molecular and band gap systems
- problematic for interaction with metal surfaces

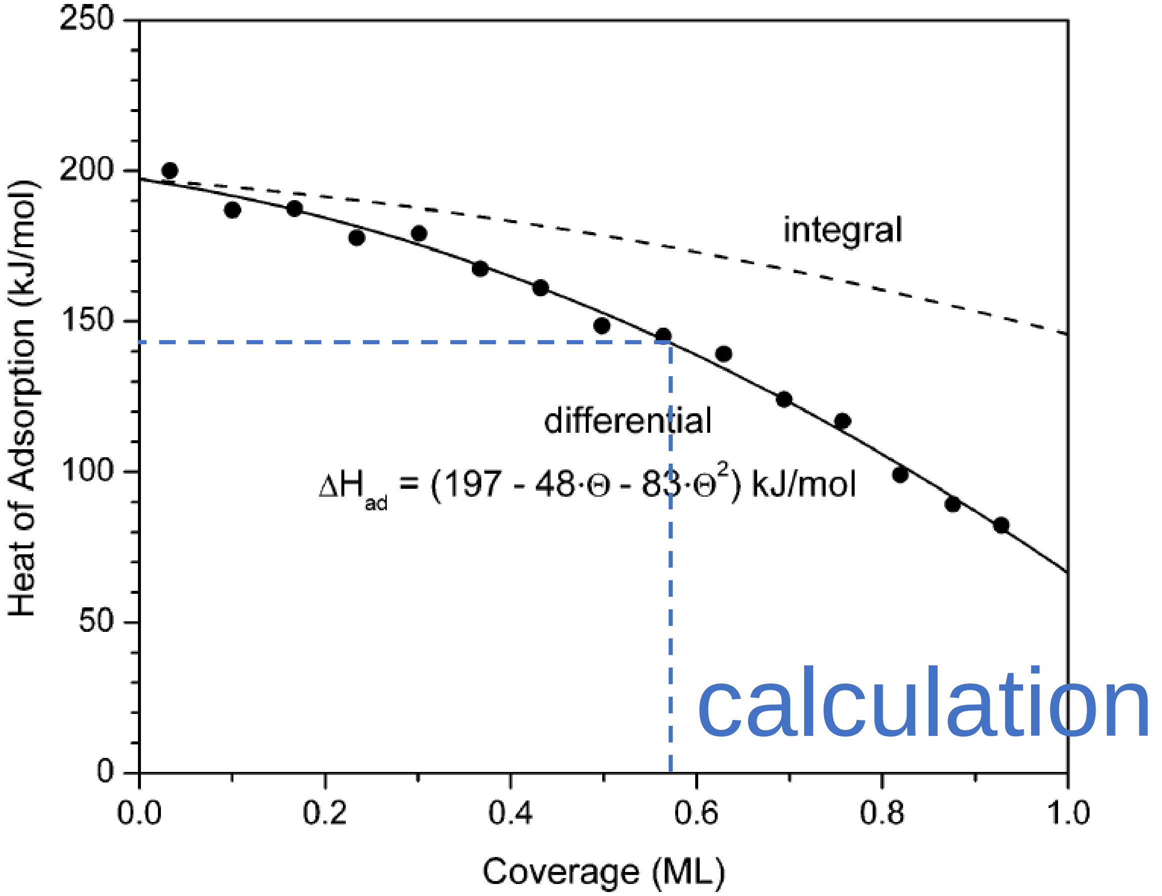
RPA is the 'best' tool for heterogeneous catalysis

- but computationally out of reach

Typical challenges: 3.coverage dependence

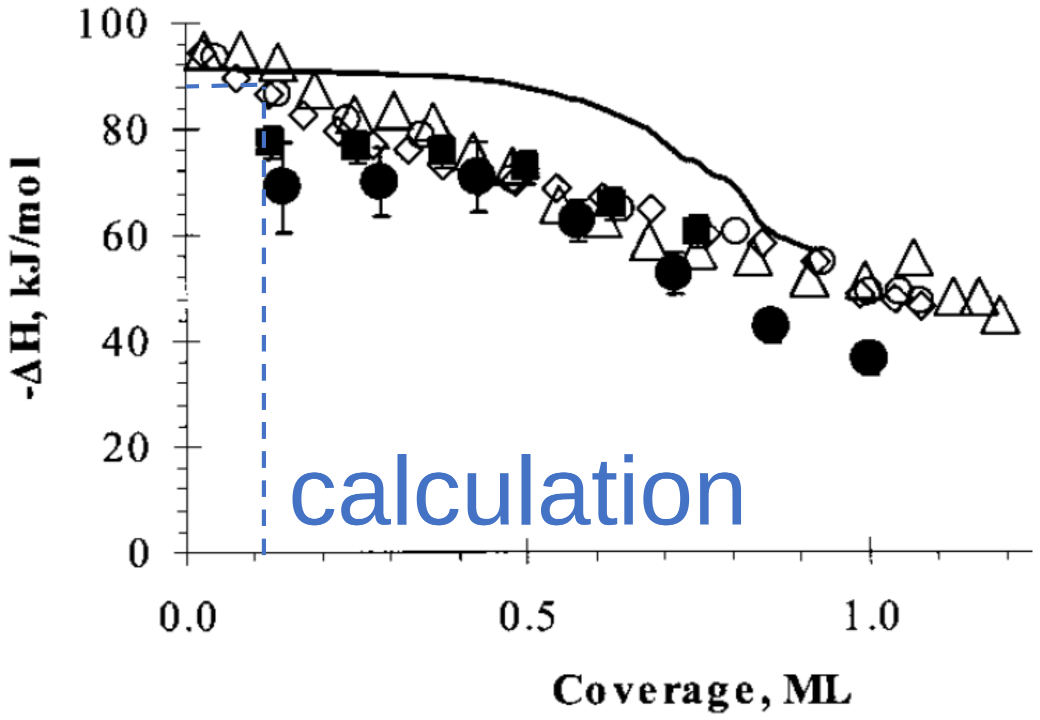
Experimental data shows that adsorption enthalpies are strongly coverage dependent

Benzene adsorption energy $\Delta_{ads}H(B)(\theta_B)$



Ihm et al, *J. Phys. Chem. B* **2004,** *108:* 14627

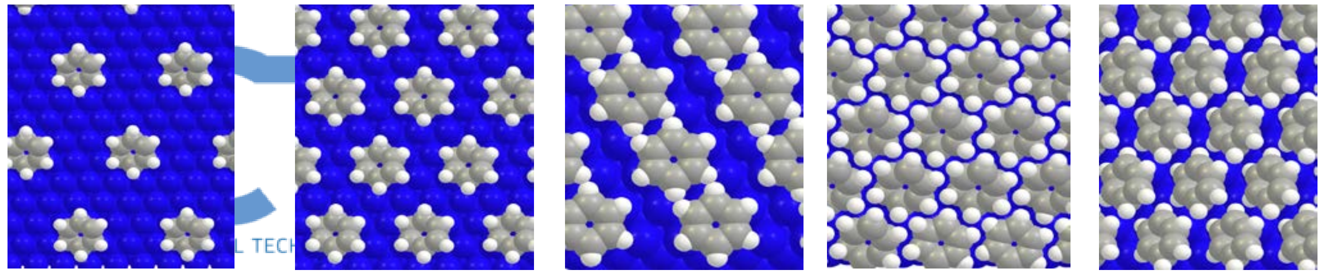
H_2 adsorption energy $\Delta_{ads}H(H_2)(\theta_B)$
(differential)

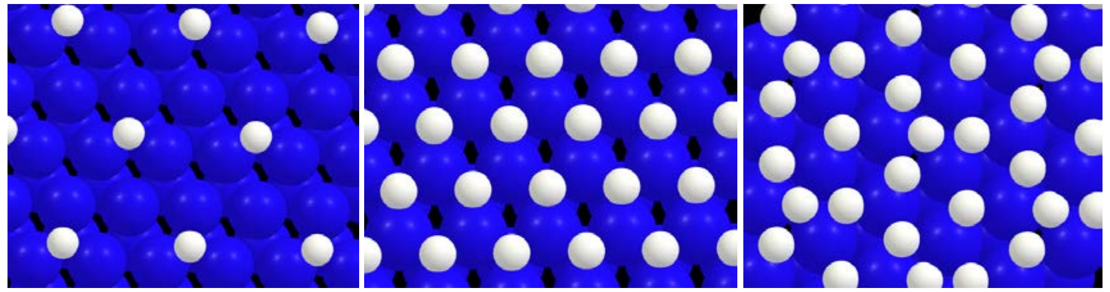


Podkolzin et al. *JPCB*, 2001, 105:8550

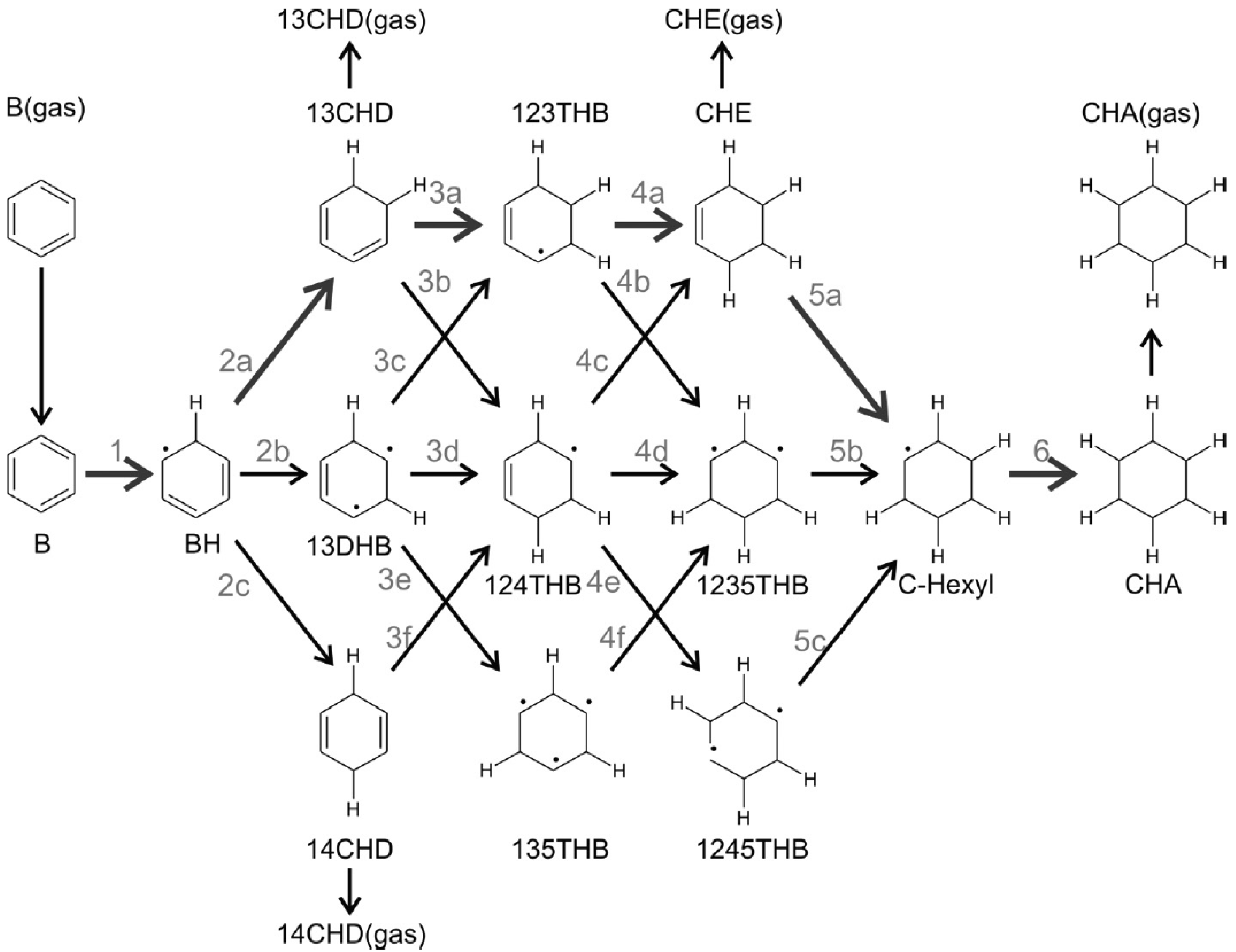
Pt(111) single crystal, 300 K

300 K, Pt/SiO_2 (low and high dispersion), Pt powder,
Pt(111) by nuclear and recoil scattering

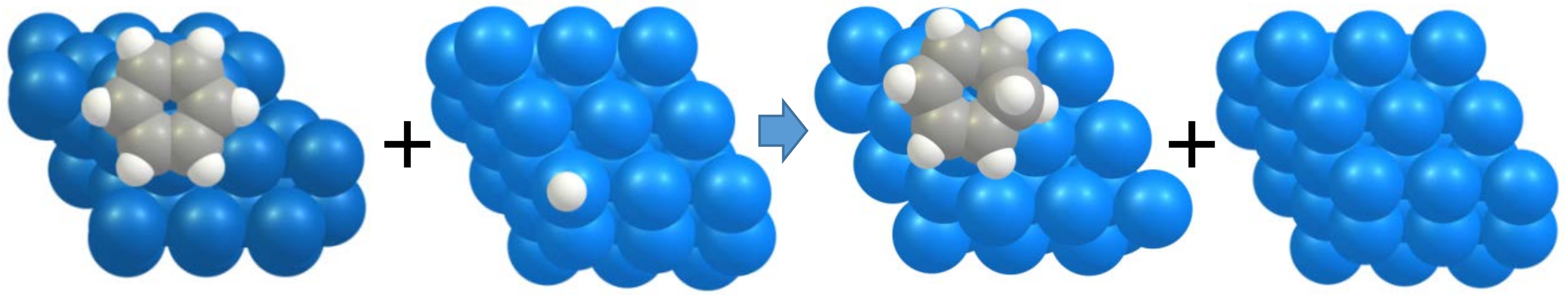




Case: benzene hydrogenation on Pt(111)



Kinetics at low coverage: ortho path dominant

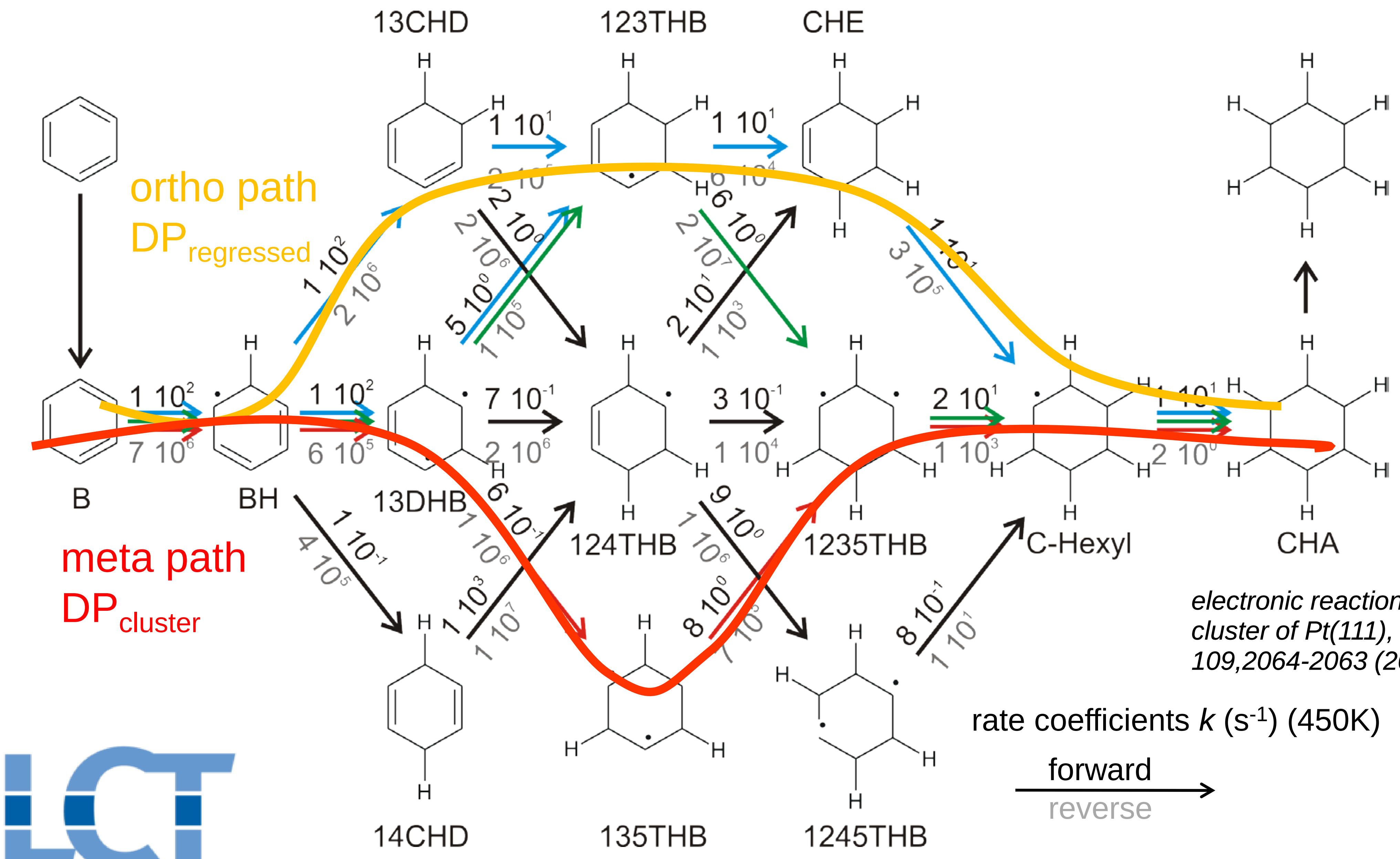


DP$_{cluster}$

minimum energy path (periodic Pt(111))

PW91 functional

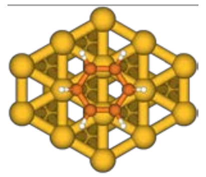
DP based on μ-kinetic simulation



ortho path: Bera T, et al.I&EC research, 50,12933 (2011)

DP in agreement with path obtained by regression to exptl data

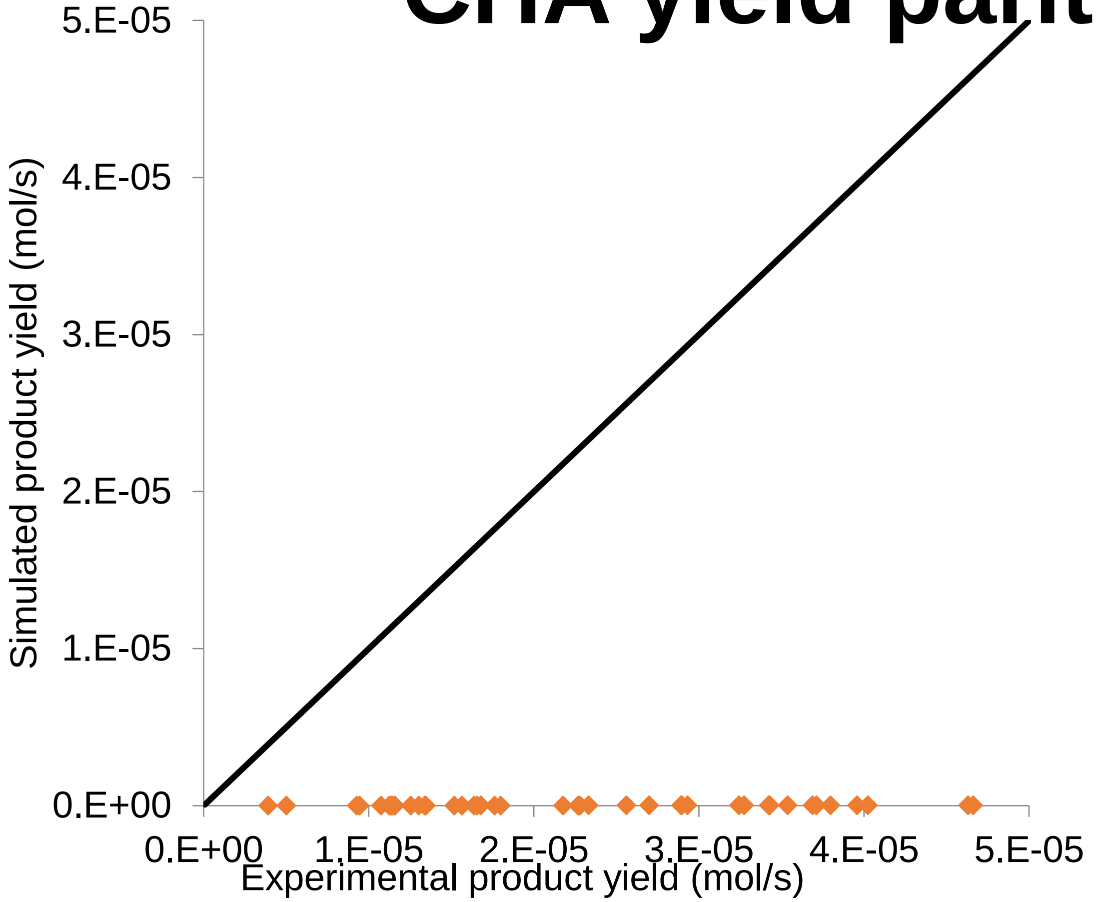
electronic reaction barriers BP86/DZ on Pt$_{22}$ cluster of Pt(111), Saeys et al,J.Phys.Chem.B, 109,2064-2063 (2005)



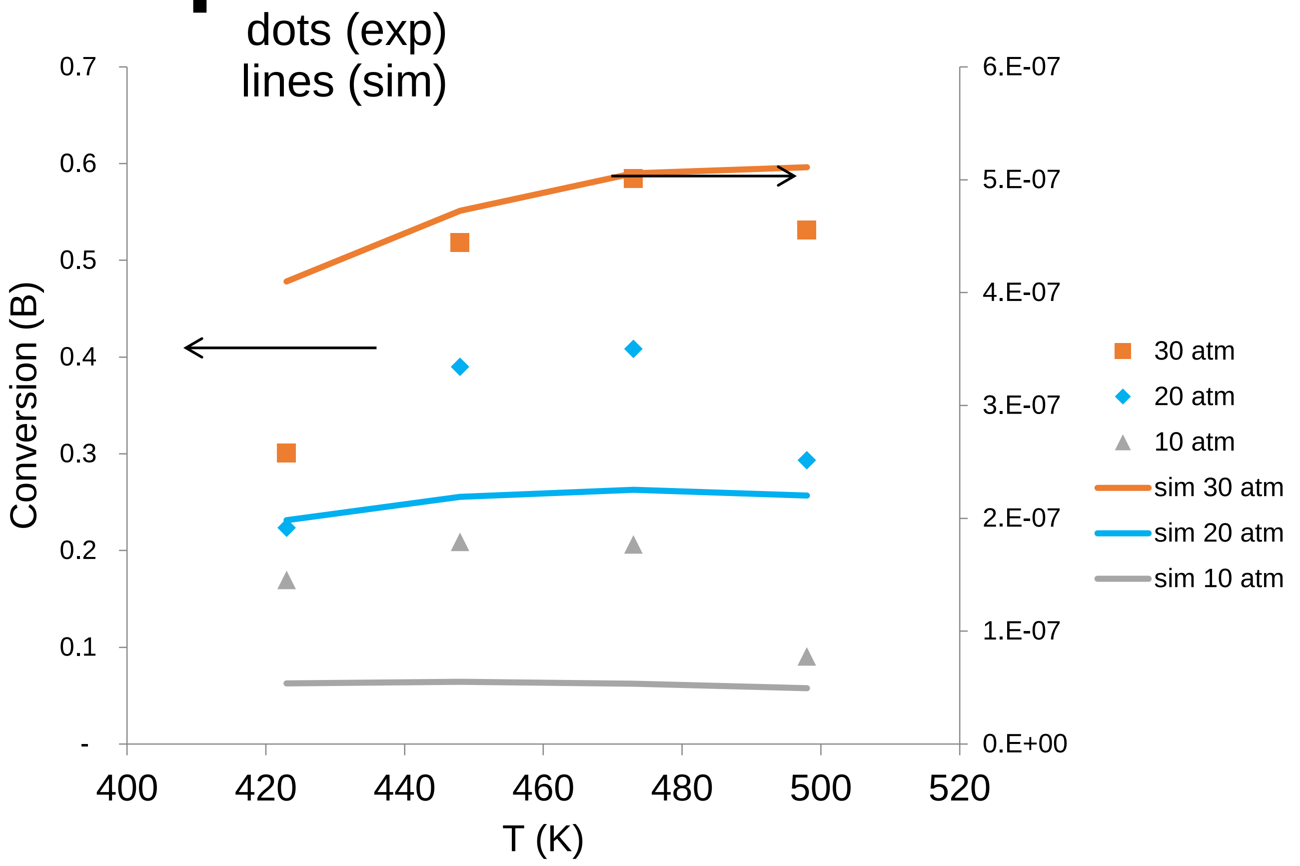
benzene adsorbed at hollow adsorption site: more reactive than bridge (based on $\Delta^{\ddagger}E_{el}$)

PW91, low coverage: too low TOF's

CHA yield parity plot



T-dependence of conversion (2 scales)



Property	Experiment	Simulated
Range R_{CHA} (mol/s)	$4\ 10^{-6}$ - $5\ 10^{-5}$	$7\ 10^{-13}$- $6\ 10^{-11}$
n_{H2} (p_{tot} = 30 atm, pB = 0.6 atm)	0.45 - 0.69	0.69 - 1.02
n_B (p_{H2} = 3 atm)	−0.04 - −0.32	0.94 - 1.00

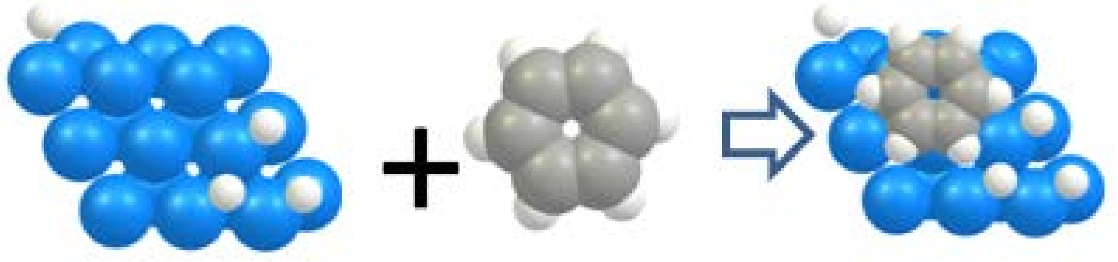
- rates 6-7 orders of magnitude too low
- incorrect temperature dependence
- partial reaction orders too high, and wrong sign for benzene

GHENT UNIVERSITY

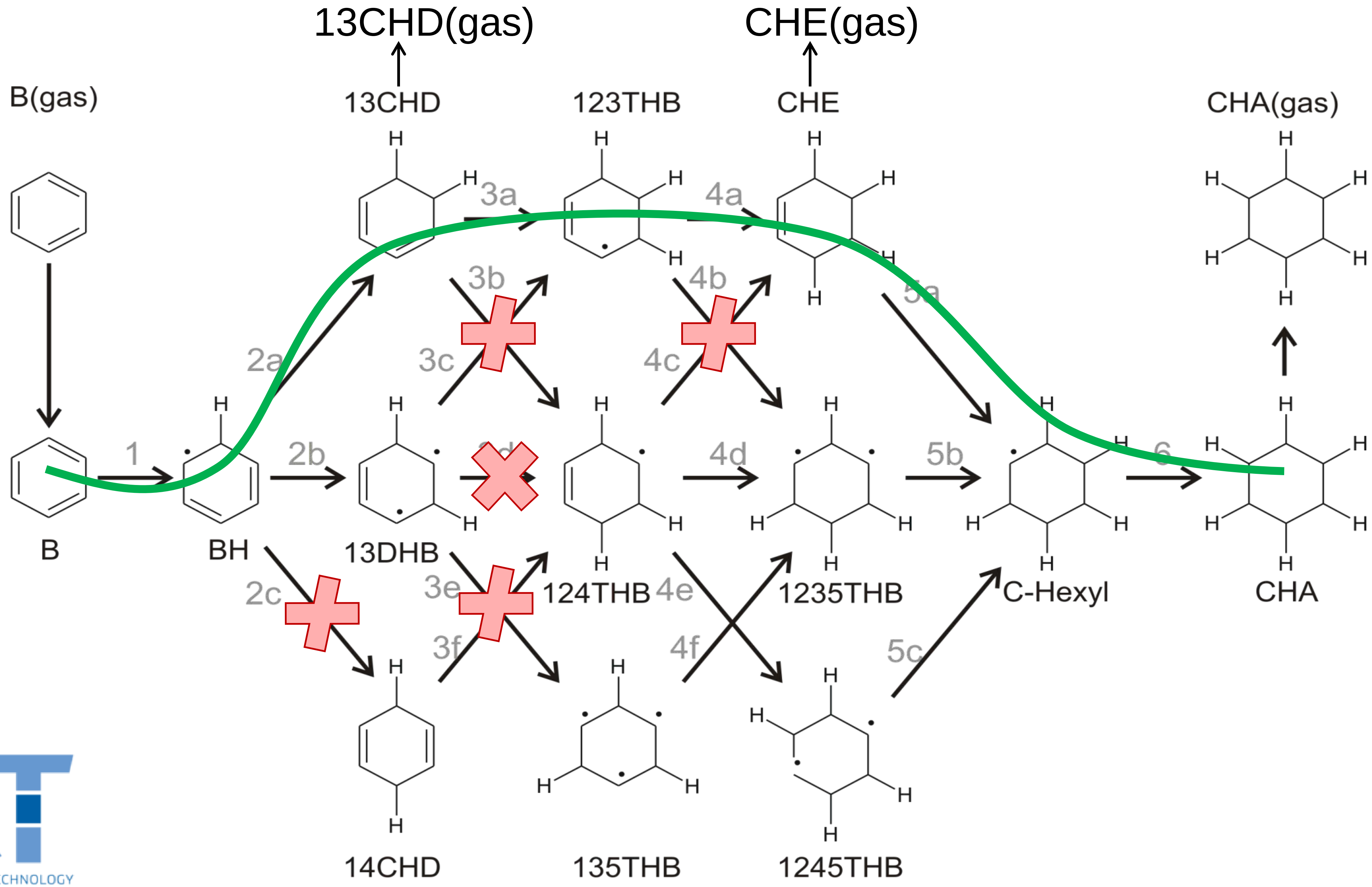
DRIVING CHEMICAL TECHNOLOGY

Sabbe et al., JCat, 330(2015):406

Kinetics at θH = 0.44: ortho path dominant

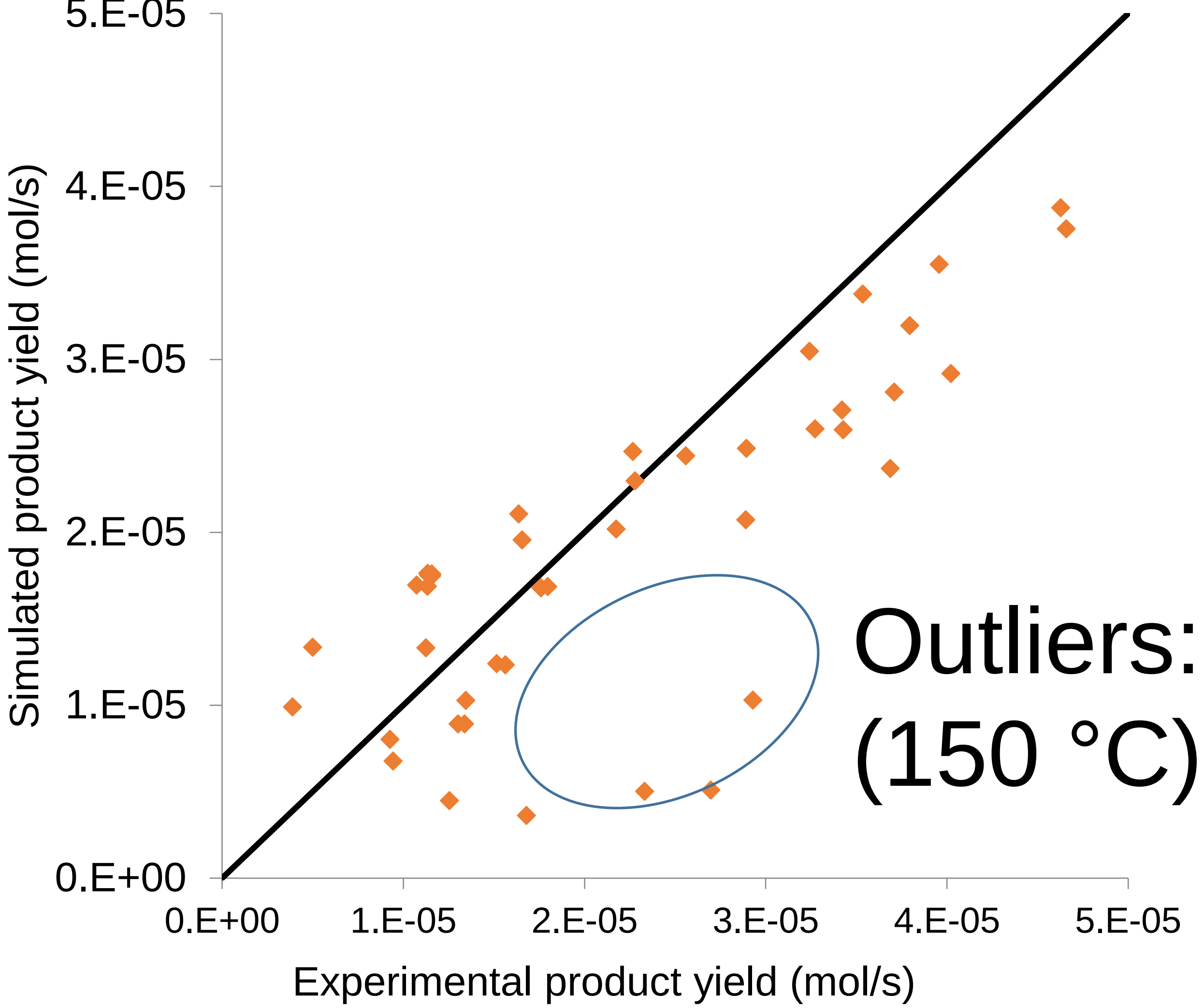


optPBE vdw-DF functional



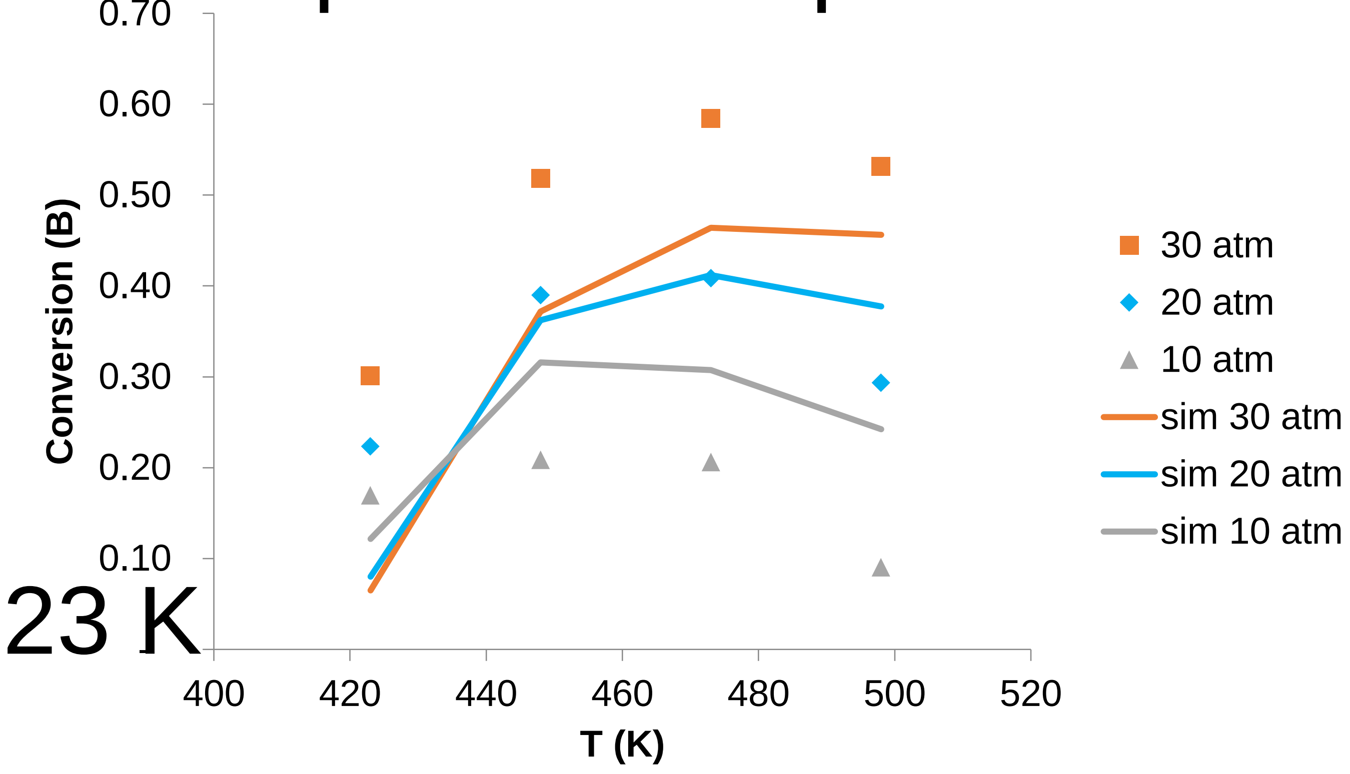
vdw-DF, θH = 0.44: good agreement

Cyclohexane product yield



Outliers: 423 K (150 °C)

Temperature dependence of conversior



	Experiment	Simulated
Range R_{CHA} (mol/s)	$4\ 10^{-6}$ - $5\ 10^{-5}$	$4\ 10^{-6}$ - $4\ 10^{-5}$
n_{H2} (p_{tot} = 30 atm, pB = 0.6 atm)	0.45 - 0.69	0.49 – 0.64
n_B (p_{H2} = 3 atm)	−0.04 - −0.32	−0.32 - −1.02

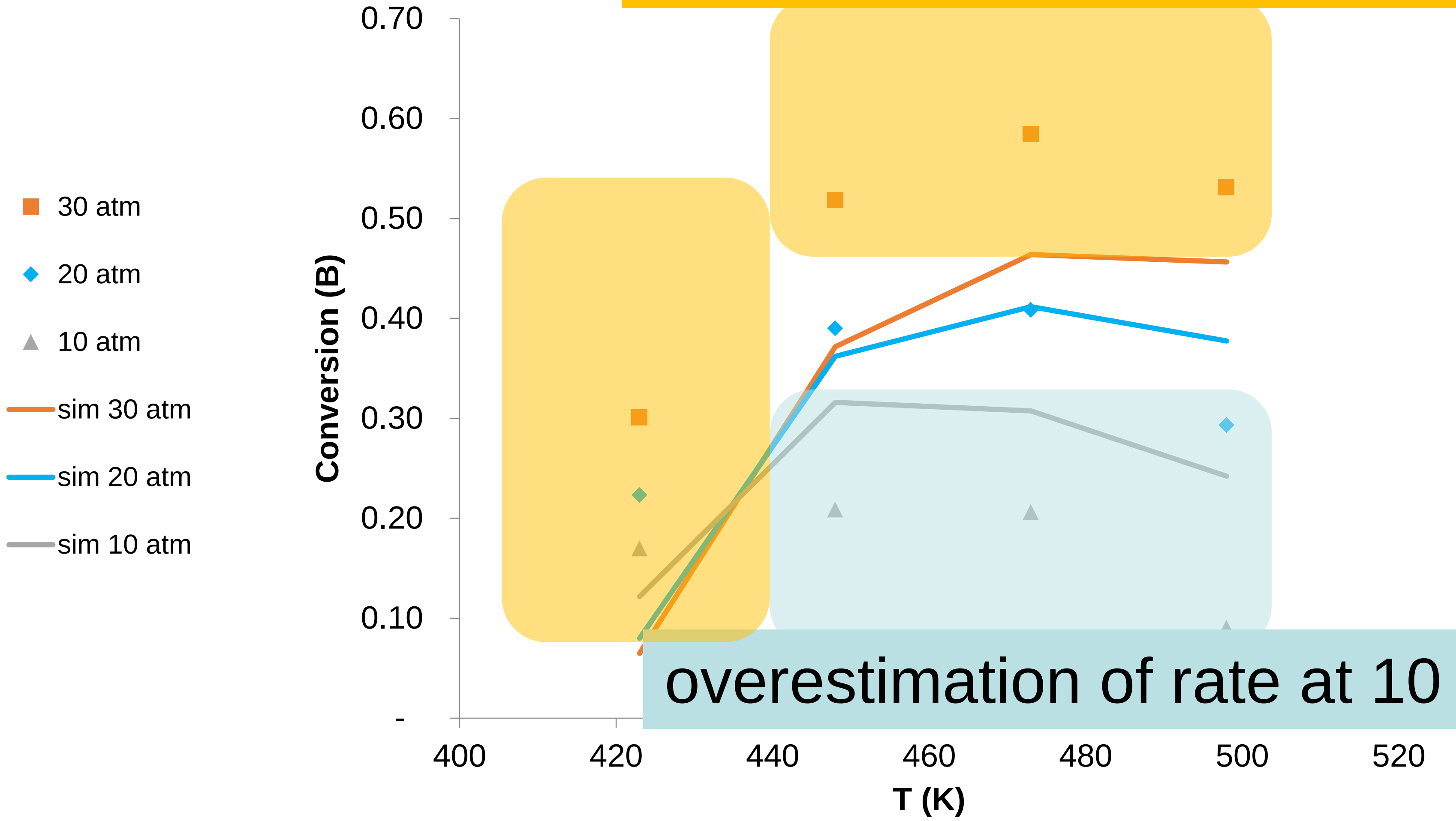
- Fair agreement to experimental product yields and captures trends
- Correct qualitative behavior of conversion vs. *T*
- Partial reaction orders:
    - For H_2 close to experiment
    - For benzene too low
- Selectivity: only CHA if T > 450K

Sabbe et al., JCat, 330(2015):406

Can this be further improved?

Temperature dependence of conversion

underestimation of rate at 30 atm



overestimation of rate at 10 atm

underestimation of rate at low T

conditions corresponding to H coverages $\theta_H > 0.44$?

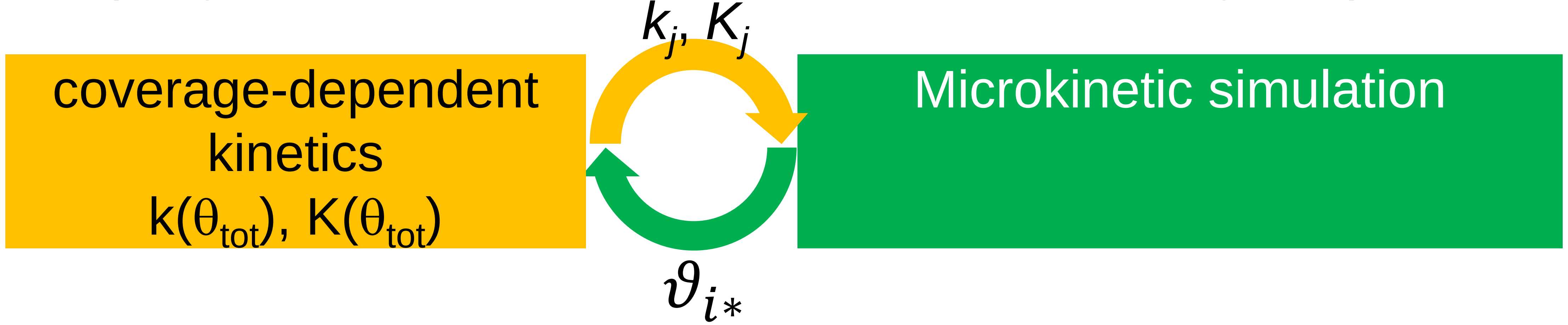
conditions corresponding to H coverages $\theta_H < 0.44$?

is a dynamic, explicit coverage dependence as function of the conditions required ?

already evaluated for benzene hydrogenation on Pd(111)

Dynamic coverage-dependent kinetics on Pd(111)

Coupling between microkinetic simulation & coverage-dependent kinetics



k_j, K_j

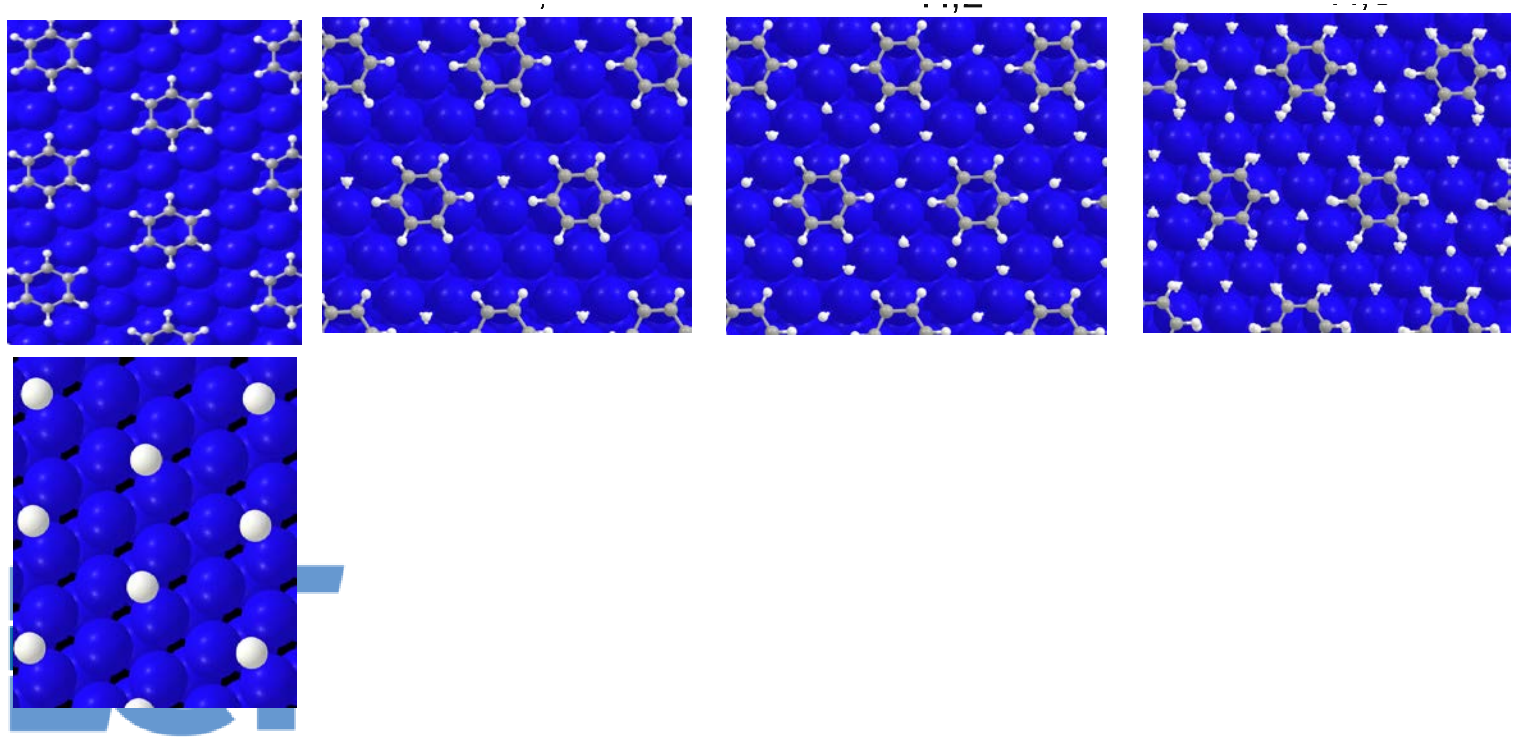
coverage-dependent kinetics $k(\theta_{tot})$, $K(\theta_{tot})$

Microkinetic simulation

ϑ_{i*}

Rate coefficients calculated at 4 coverages:

$\theta_H = 0.11$	$\theta_H = 0.11$	$\theta_H = 0.44$	$\theta_H = 0.67$
$\theta_{tot} = 0.11$	$\theta_{tot} = 0.22$	$\theta_{tot} = 0.55$	$\theta_{tot} = 0.78$

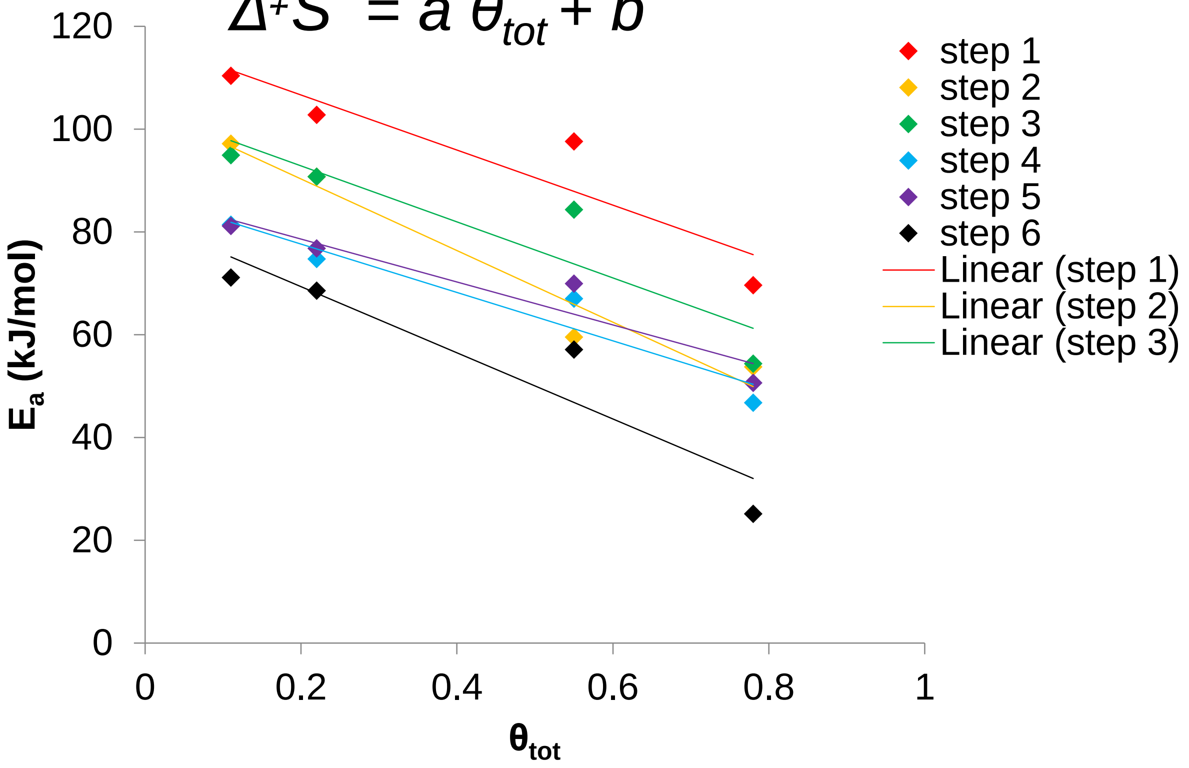


Regression of linear relations to kinetic parameters at 4 coverages

For every reaction step:

$E_a = a\,\theta_{tot} + b$

$\Delta^{\ddagger}S = a\,\theta_{tot} + b$

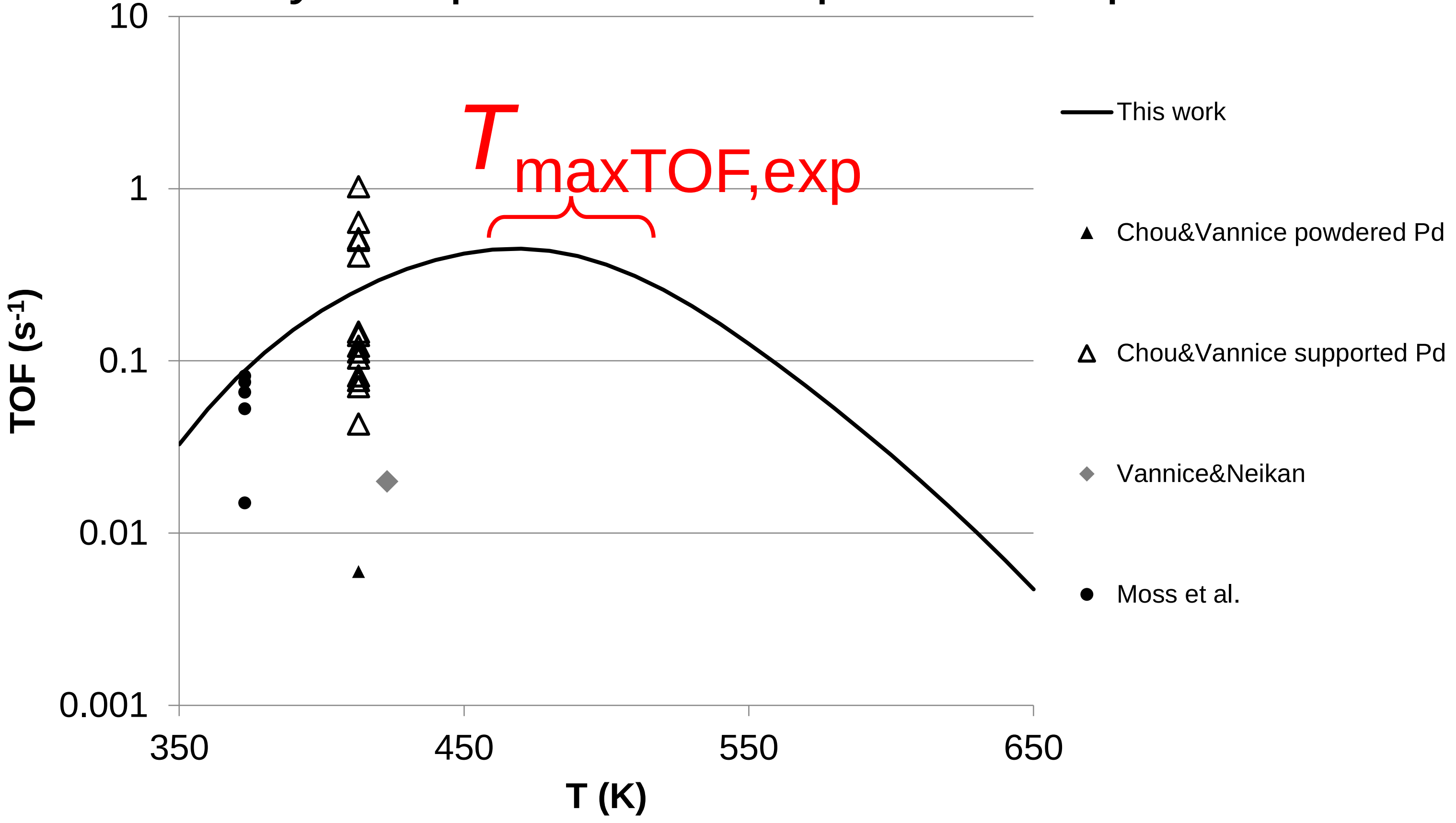


GHENT UNIVERSITY

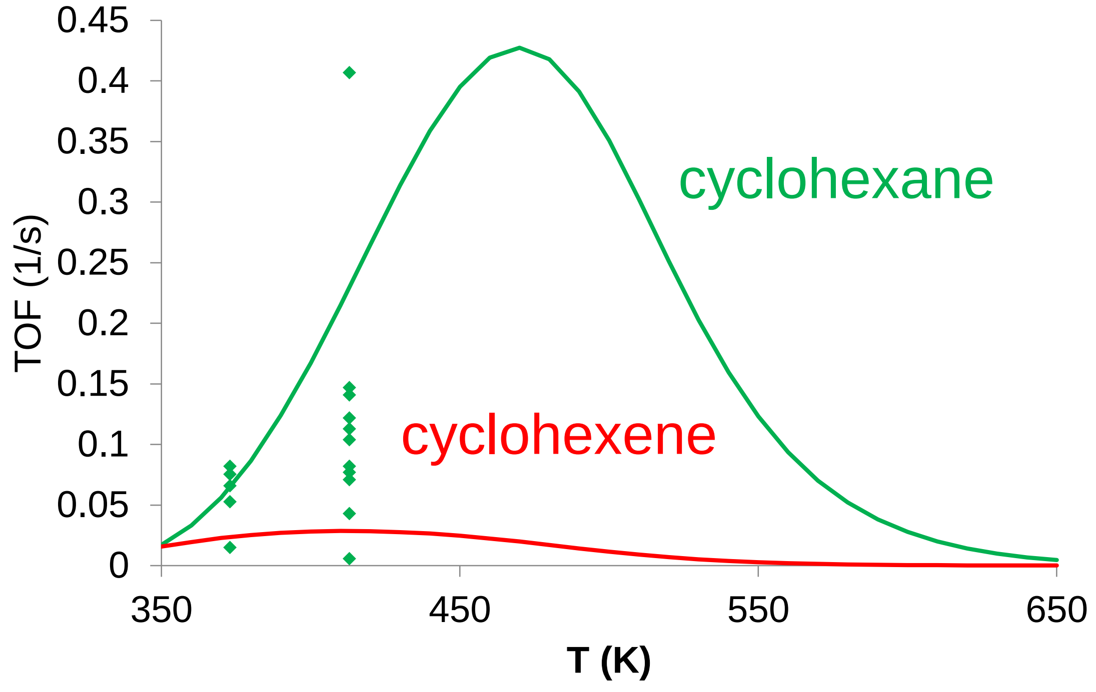
DRIVING CHEMICAL TECHNOLOGY

Dynamic coverage-dependent kinetics on Pd(111)

Activity well predicted compared to experiment



Selectivity well predicted for T > 400 K



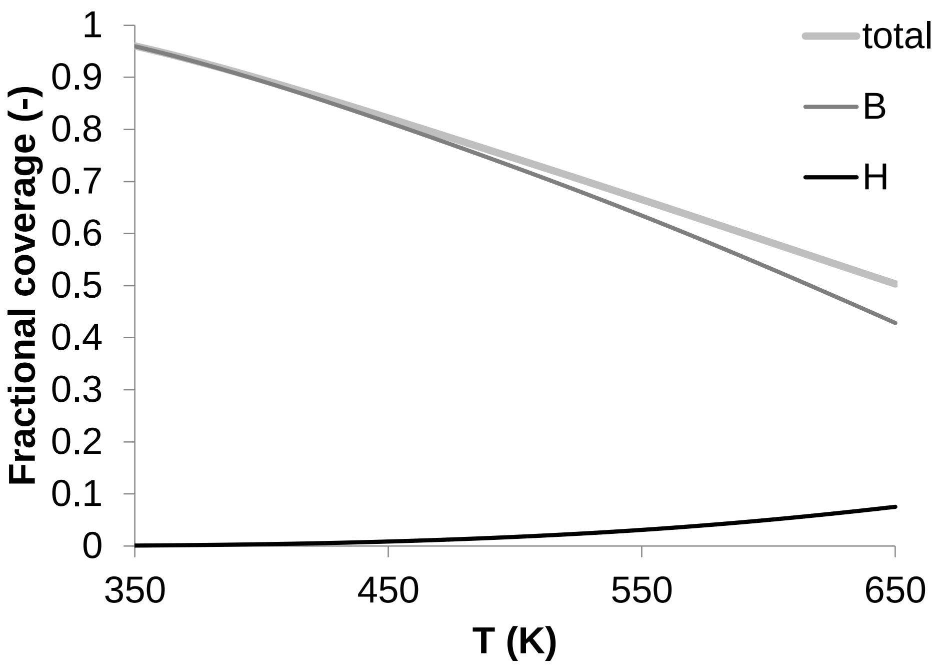
Chou & Vannice J.Cat., 107 (1987):129-139
Vannice & Neikam J.Cat., 23 (1971) 401-405
Moss et al., J.Cat., 58 (1979) 206-219

	experiment[a]	Simulated
Range R_{CHA} (mol/s)	6×10^{-3} - 1.1	0.2
n_B	−0.5 - −0.2	-0.02
n_{H2}	~1	1.2

413 K, p_{H2}= 0.9 bar, p_B= 6.6×10^{-2} bar

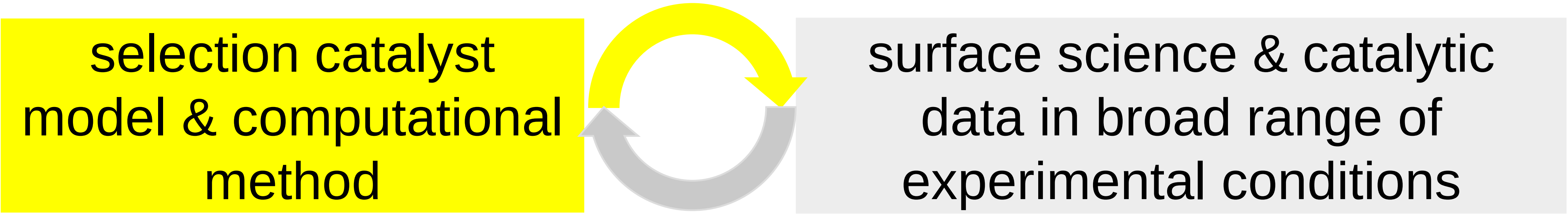
[a] *Chou & Vannice J.Cat., 107 (1987):129-139.*

Total coverages in range 0.5 - 1



Benzene hydrogenation: take home

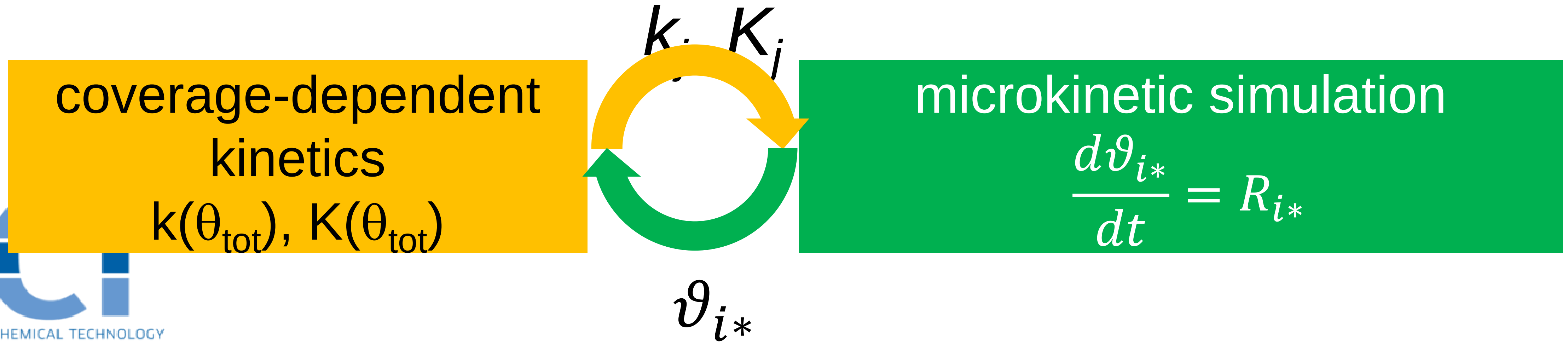
- critical selection of catalyst model, computational method and effects to be included requires benchmarking/feedback from experiment



selection catalyst model & computational method

surface science & catalytic data in broad range of experimental conditions

- accounting for explicit coverage dependence brings quantitative agreement at industrially relevant reactions conditions within reach



k_j K_j

coverage-dependent kinetics
$k(\theta_{tot})$, $K(\theta_{tot})$

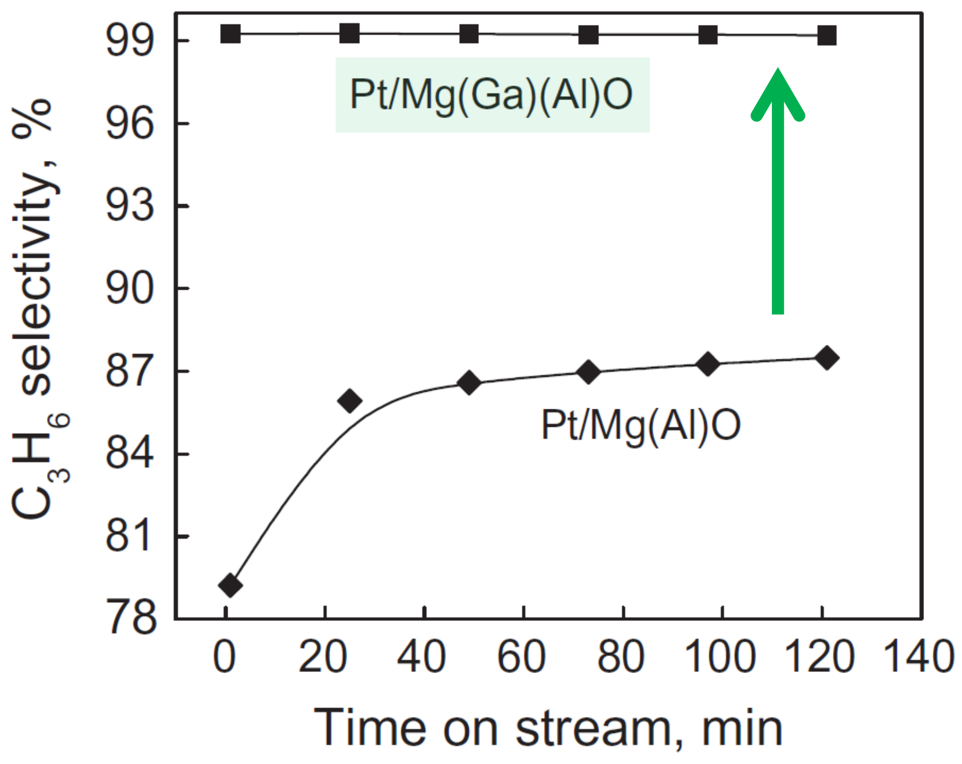
microkinetic simulation

$$\frac{d\vartheta_{i*}}{dt} = R_{i*}$$

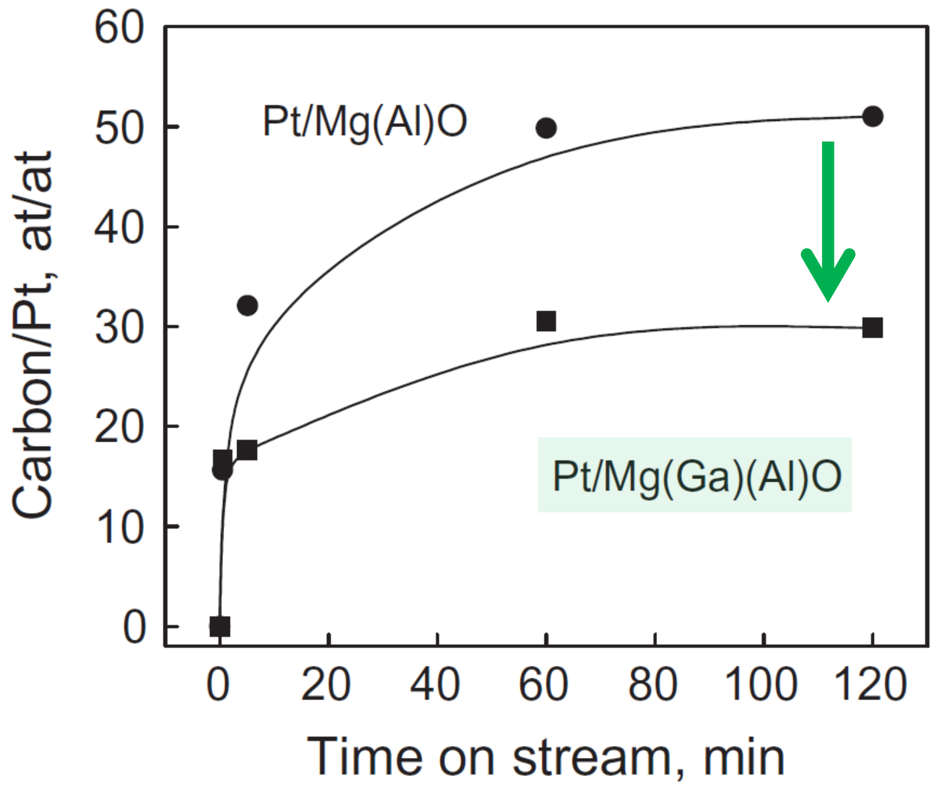
ϑ_{i*}

Case: propane dehydrogenation on Pt/Ga

Siddiqi G., Sun P.P., Galvita V., Bell A.T., Journal of Catalysis, 274 (2010).
Sun P.P., Siddiqi G., Galvita V., Bell A.T., Journal of Catalysis, 274 (2010).
Wang T., Jiang F., Liu G., Zeng L., Zhao Z.J., Gong J., AIChE Journal, 62 (2016)



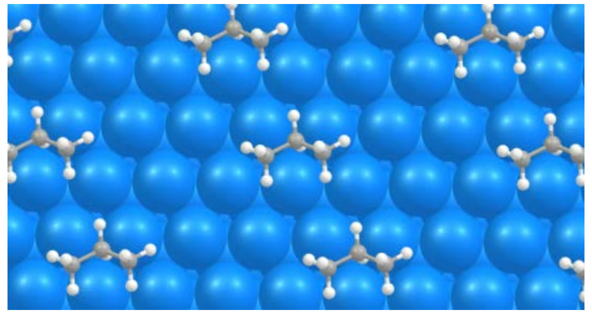
Selectivity C_3H_6 (%)

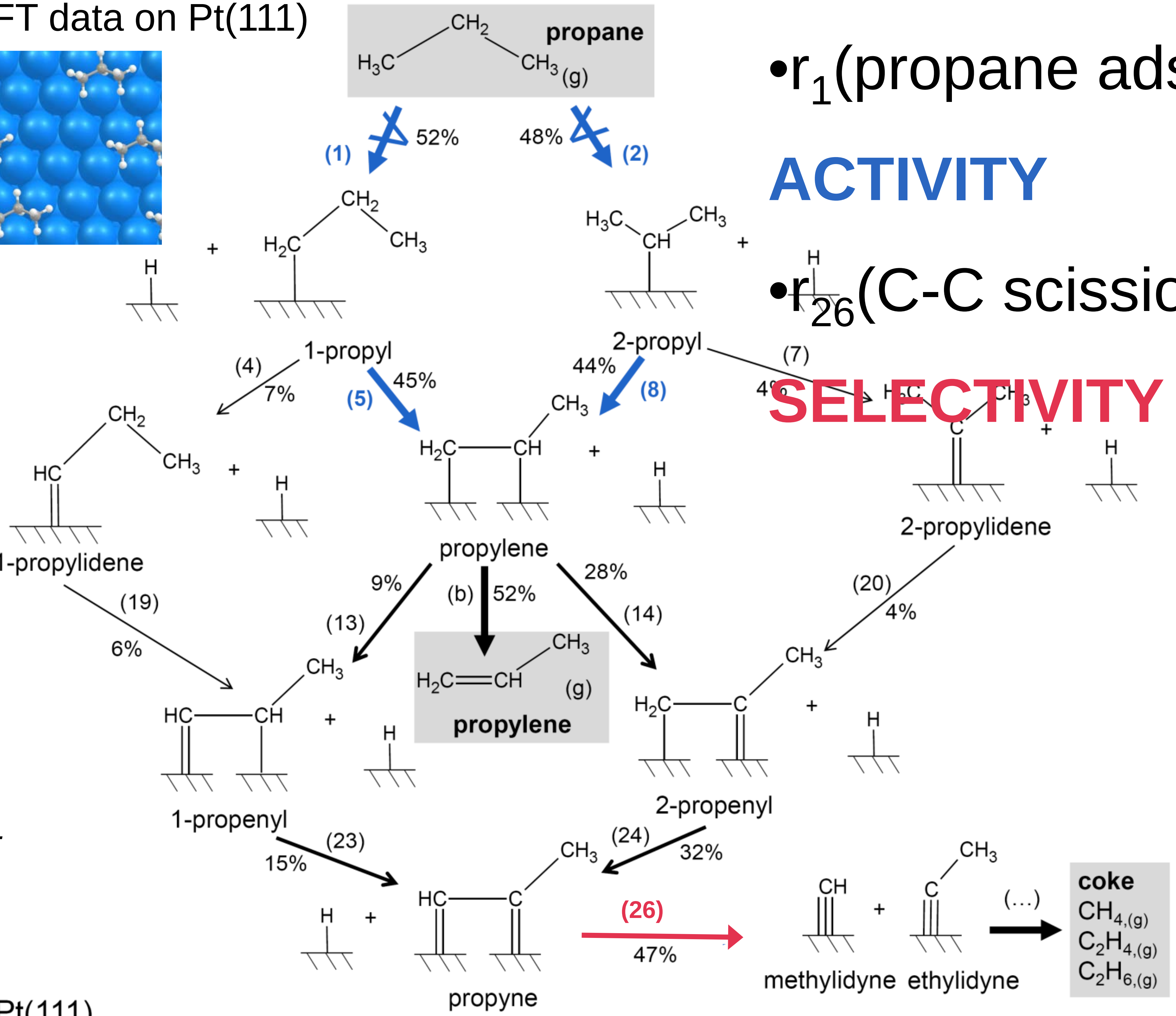


Carbon/Pt (at/at)

μ-kinetics: rate analysis on Pt(111)

based on DFT data on Pt(111)





- r_1(propane adsorption) ~

ACTIVITY

- r_{26}(C-C scission) ~

SELECTIVITY

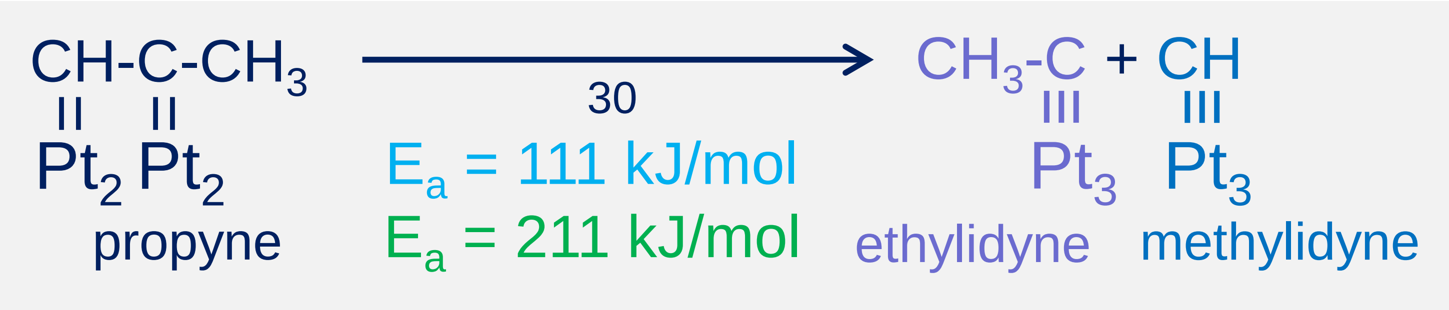
full network contains
41 elementary sterps
(forward & backward)

Saerens et al., ACS Catal.
2017, 7, 7495−7508

GHENT
UNIVERSITY

Pt(111)

C-C scission on Pt3Ga vs Pt



$$\underset{\text{propyne}}{\underset{Pt_2\;\;Pt_2}{\overset{\text{CH-C-CH}_3}{\text{II}\quad\text{II}}}} \xrightarrow[\substack{E_a = 111\text{ kJ/mol} \\ E_a = 211\text{ kJ/mol}}]{30} \underset{\text{ethylidyne}}{\underset{Pt_3}{\overset{CH_3\text{-C}}{\text{III}}}} + \underset{\text{methylidyne}}{\underset{Pt_3}{\overset{CH}{\text{III}}}}$$

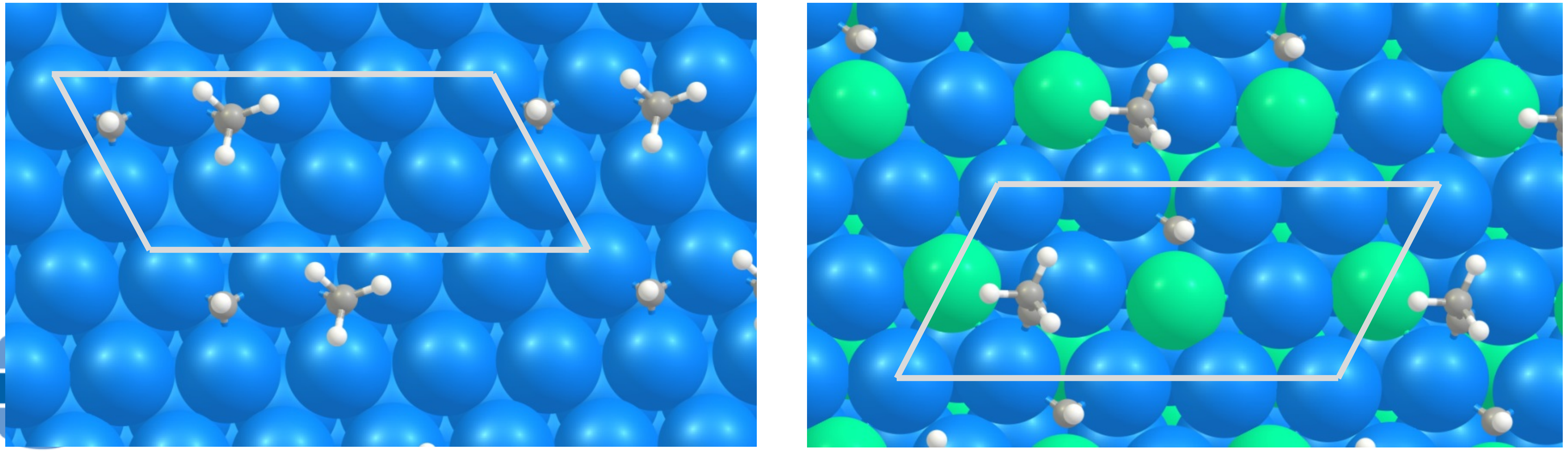
— Pt(111)

— $Pt_3Ga(111)$

High barrier for C-C scission of propyne on $Pt_3Ga(111)$

→ no formation of ethylidyne and methylidyne

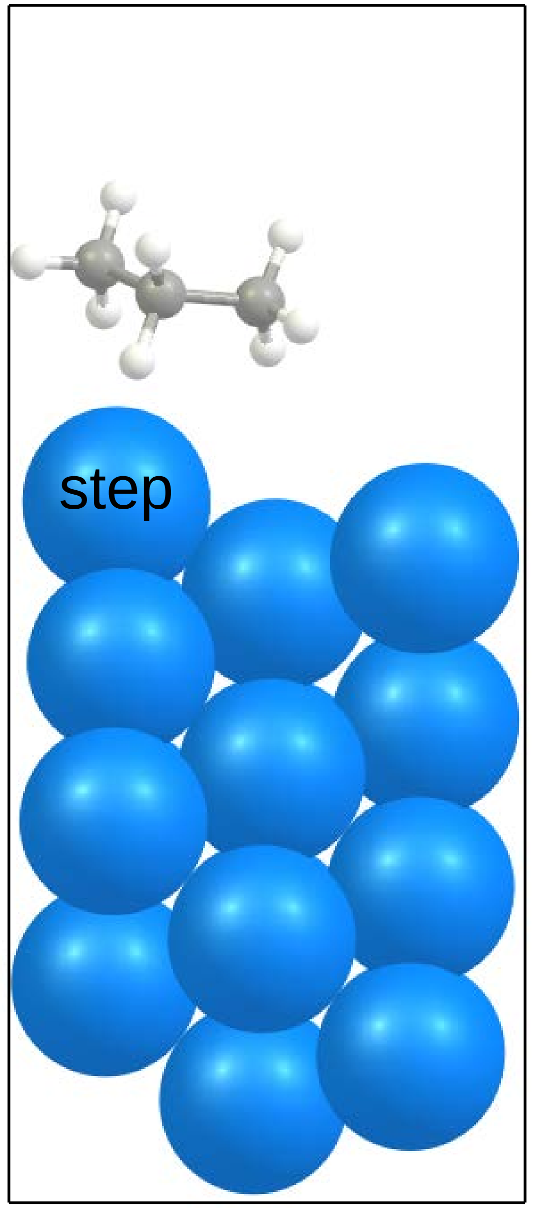
→ neglegible formation of side products coke, CH_4, C_2H_6 and C_2H_4



Coke formation on step sites?

- Pt(211) surface → include step sites

side view



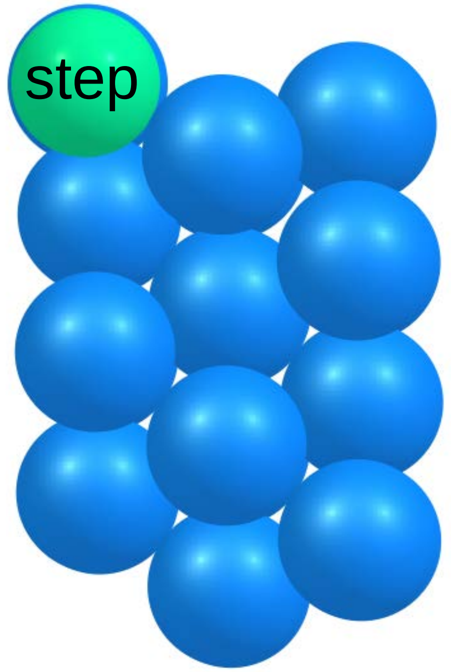
- Energetics at relevant reaction step for coke formation:

$$\underset{\text{propyne}}{\underset{\mathrm{Pt_2\ Pt_2}}{\overset{\mathrm{CH\text{-}C\text{-}CH_3}}{\text{|| \quad ||}}}} \xrightarrow[30]{} \underset{\text{ethylidyne}}{\underset{\mathrm{Pt_3}}{\overset{\mathrm{CH_3\text{-}C}}{|||}}} + \underset{\text{methylidyne}}{\underset{\mathrm{Pt_3}}{\overset{\mathrm{CH}}{|||}}}$$

Pt(111): ΔE_{elec} = -64 kJ/mol, $E_{a,elec}$ = 113 kJ/mol

Pt(211): ΔE_{elec} = -53 kJ/mol, $E_{a,elec}$ = 96 kJ/mol

- Selective blocking of defect sites by Ga atoms:



Ga prefers to sit in low-coordinated sites such as edges, kinks and steps:

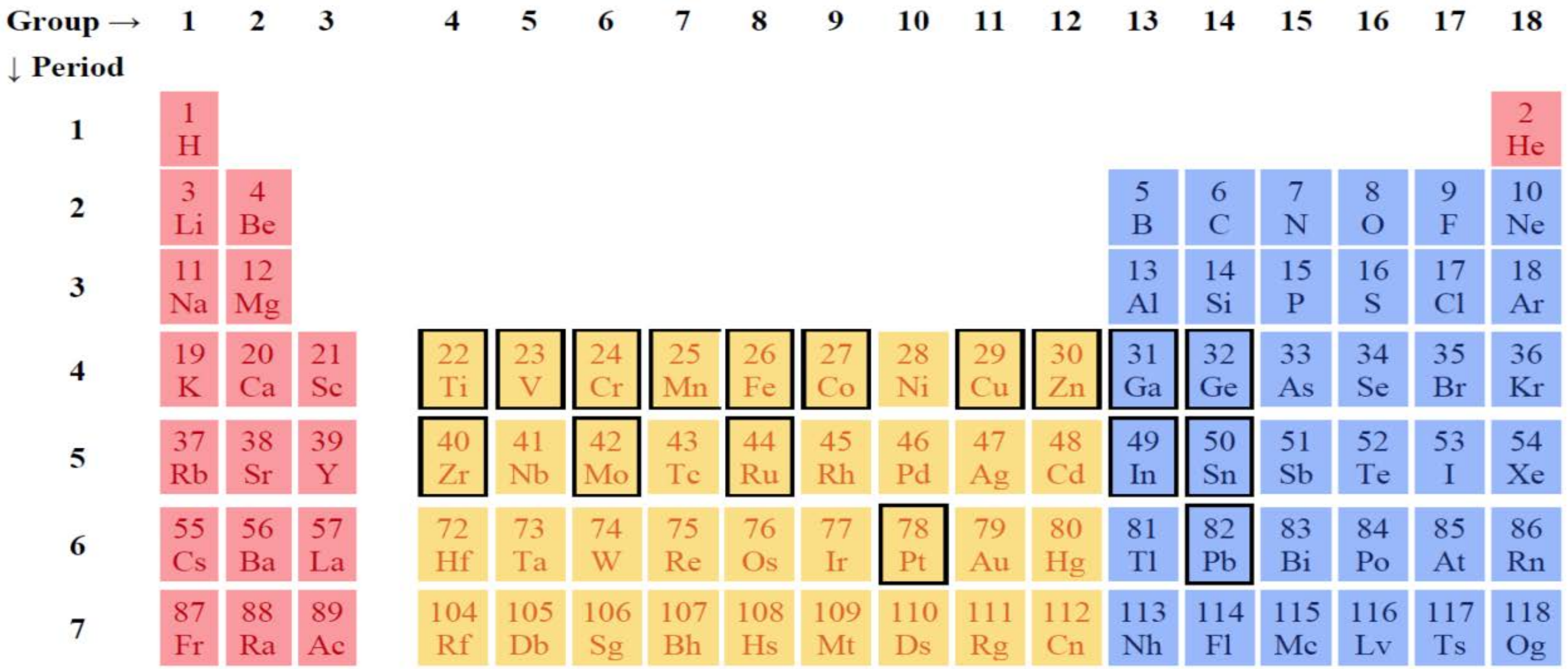
Ga on surface step → Ga in (111) surface plane
22 kJ/mol

✗ Coke formation via atomic carbon or on step sites less likely for Pt_3Ga

GHENT UNIVERSITY

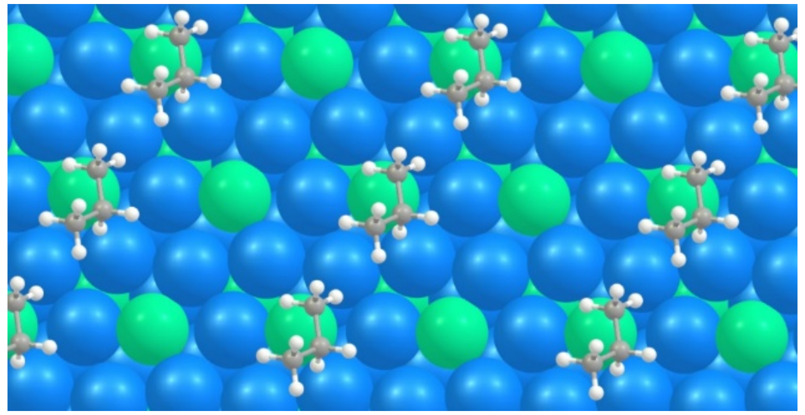
DRIVING CHEMICAL TECHNOLOGY

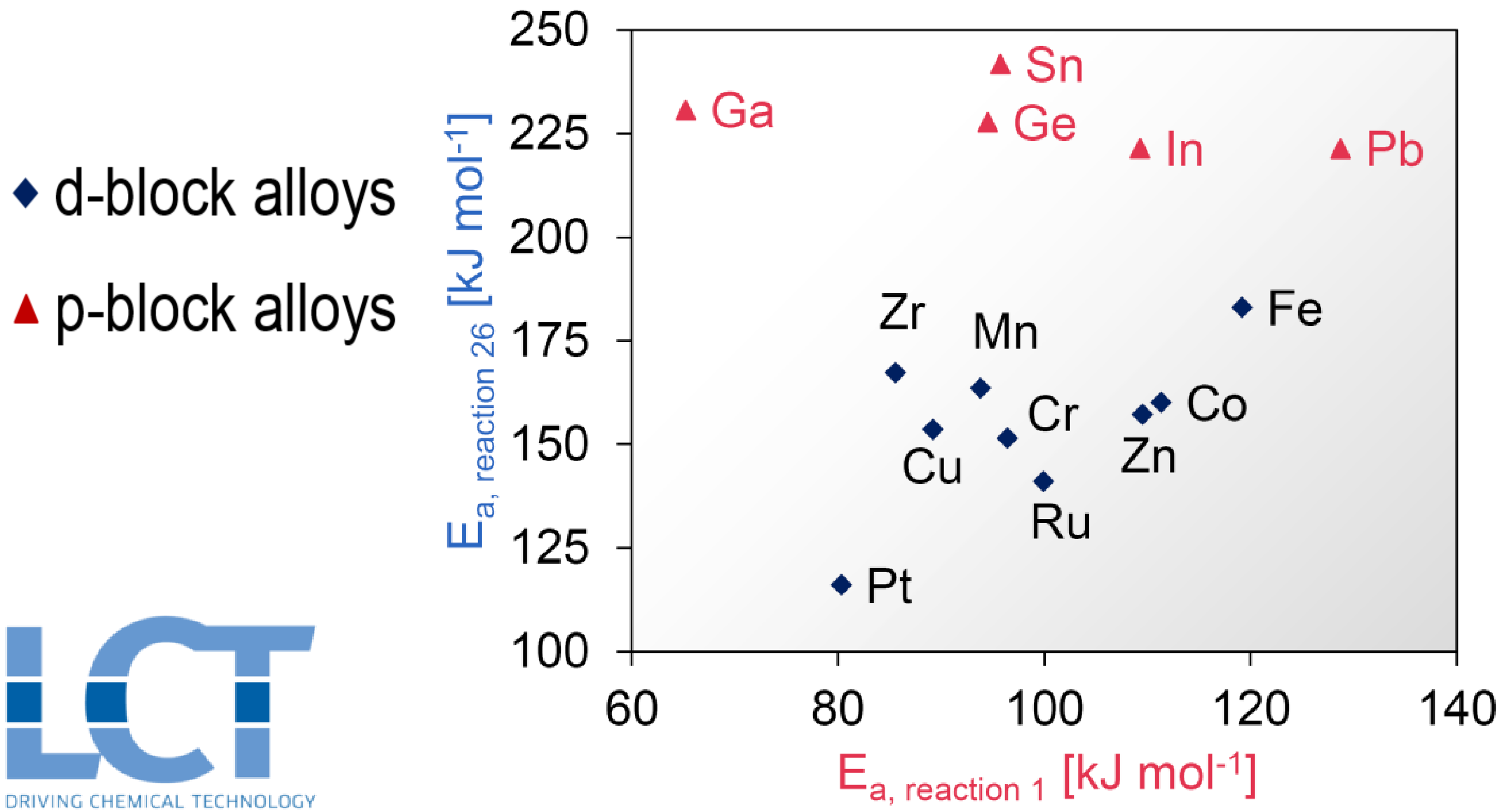
Pt3M bimetallics



Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	**22 Ti**	**23 V**	**24 Cr**	**25 Mn**	**26 Fe**	**27 Co**	28 Ni	**29 Cu**	**30 Zn**	**31 Ga**	**32 Ge**	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	**40 Zr**	41 Nb	**42 Mo**	43 Tc	**44 Ru**	45 Rh	46 Pd	47 Ag	48 Cd	**49 In**	**50 Sn**	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	**78 Pt**	79 Au	80 Hg	81 Tl	**82 Pb**	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

DFT data for all important steps on $Pt_3M(111)$



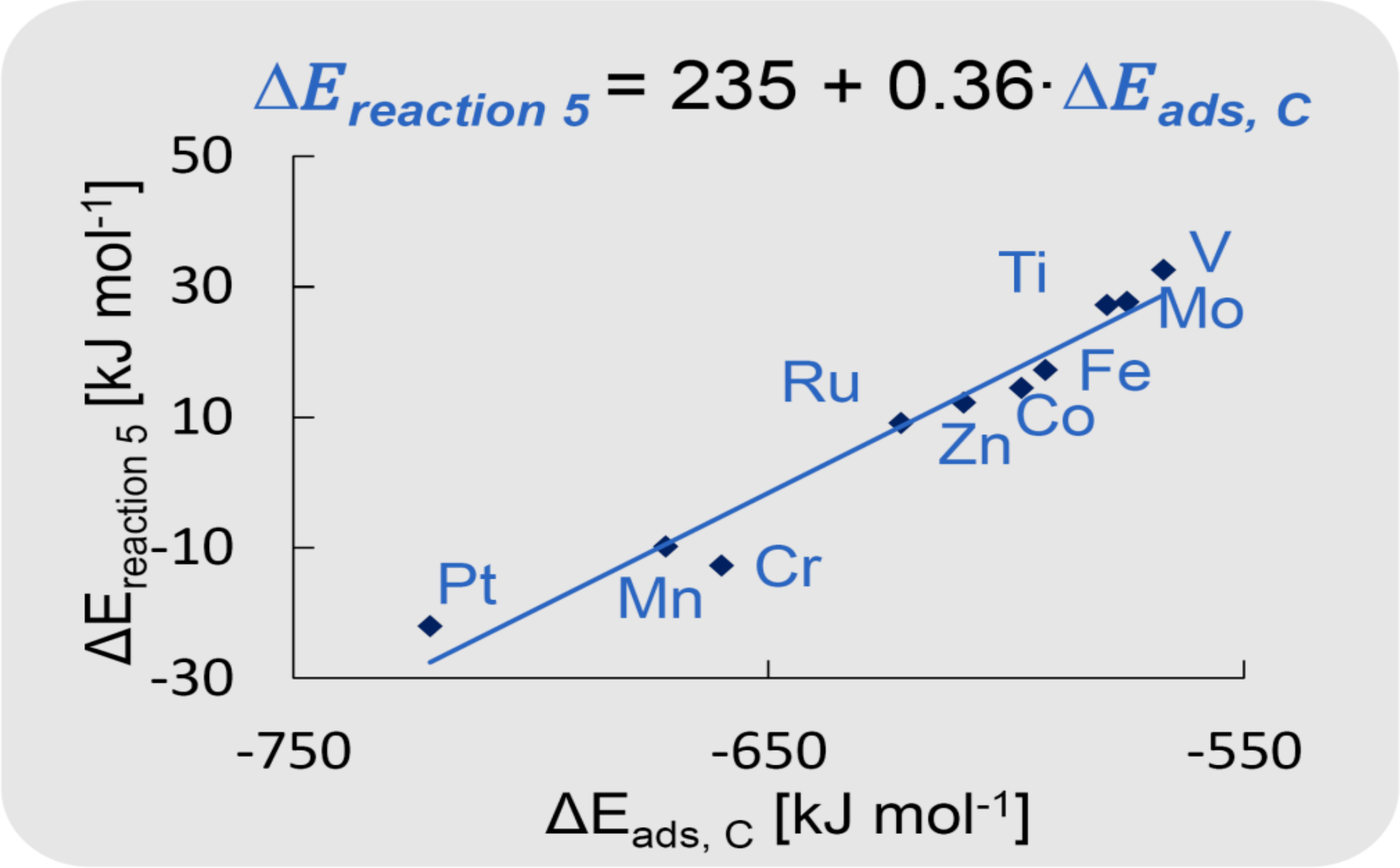


- r_1(propane adsorption) ~ **ACTIVITY**
- r_{26}(C-C scission) ~ **SELECTIVITY**

Identification of catalyst descriptor: d-block

- correlation & regression analysis of DFT data on all important reaction steps
- d-block alloys: a single descriptor can be used for all reactions; $\Delta E_{ads,C}$ works best

$$\Delta E_{r,i}/E_{a,i} = \alpha_i + \beta_i \cdot \Delta E_{ads,C}$$

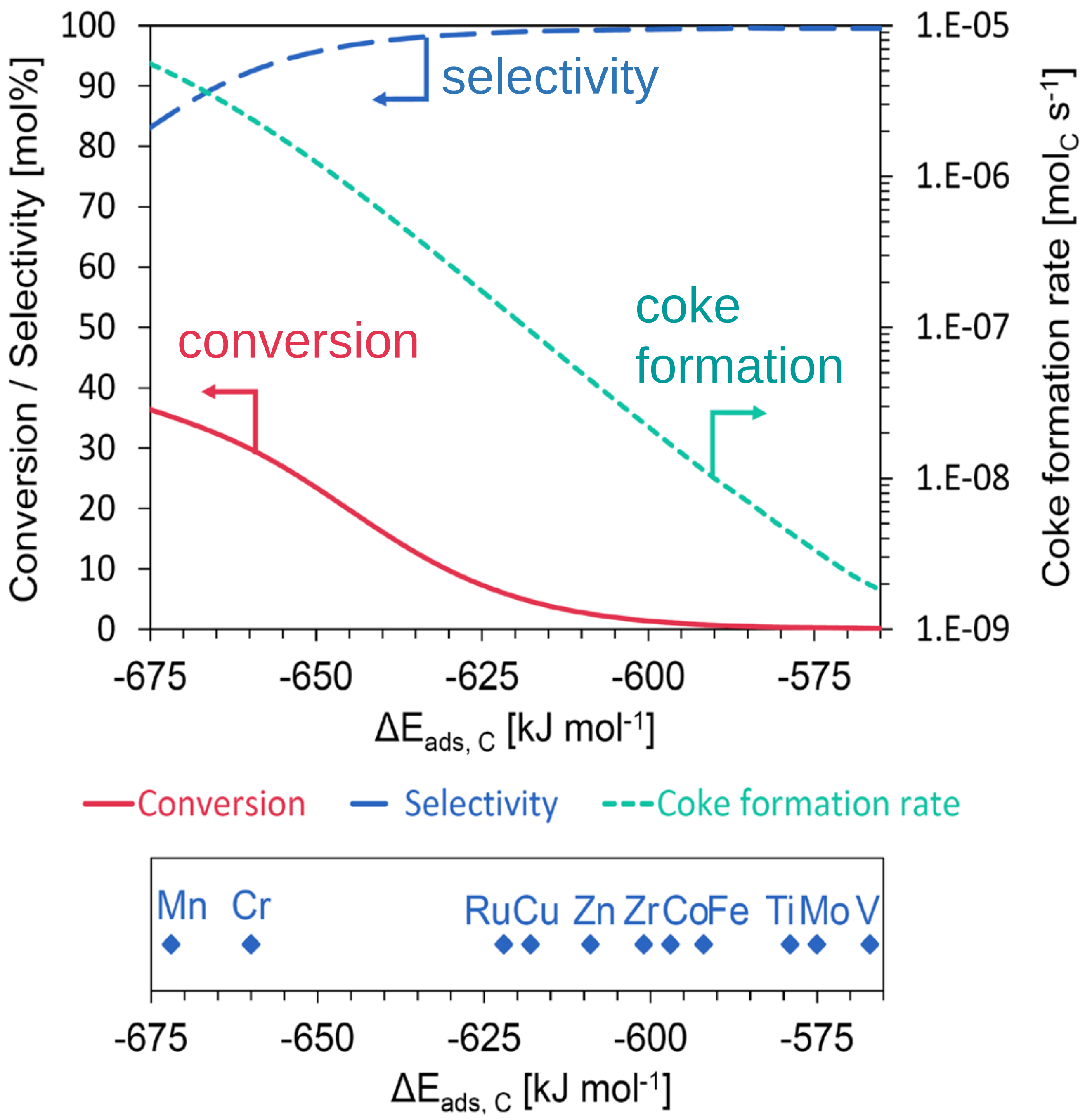


example: $\Delta E_{ads,\ reaction\ 5} = f(\Delta E_{ads,C})$

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

μ-kinetic mapping: d-block



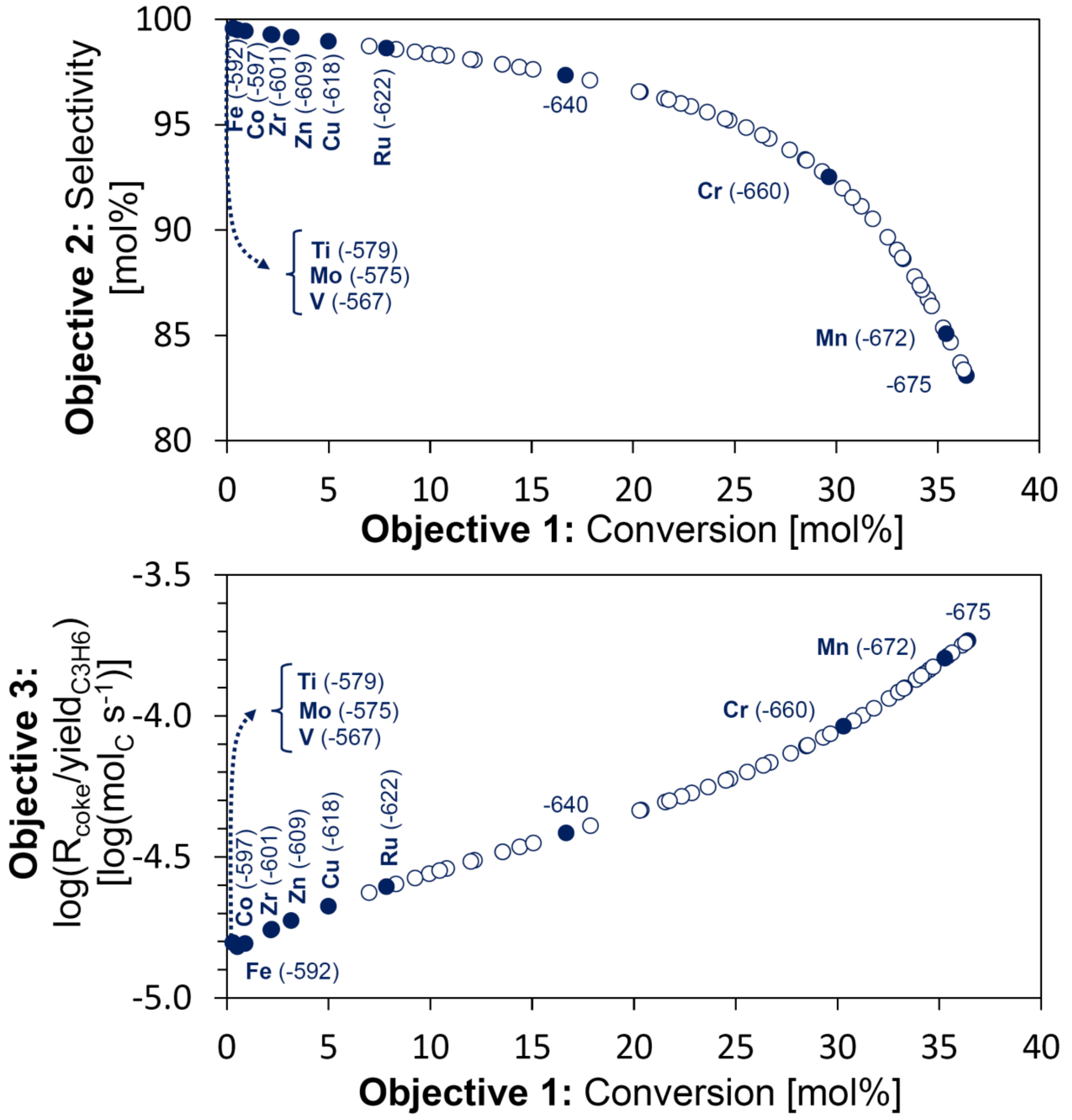
(T = 600 °C, p = 1 atm, $WHSV$ = 882 h^{-1})

- *strong* carbon adsorption
  - ⇒ high activity
- *weak* carbon adsorption
  - ⇒ high selectivity
  - ⇒ good anti-coking ability

Multi-objective optimization: d-block

optimal trade-offs between catalytic activity, selectivity and anti-coking ability = f(descriptor)

(T = 600 °C, p = 1 atm, $WHSV$ = 882 h^{-1})

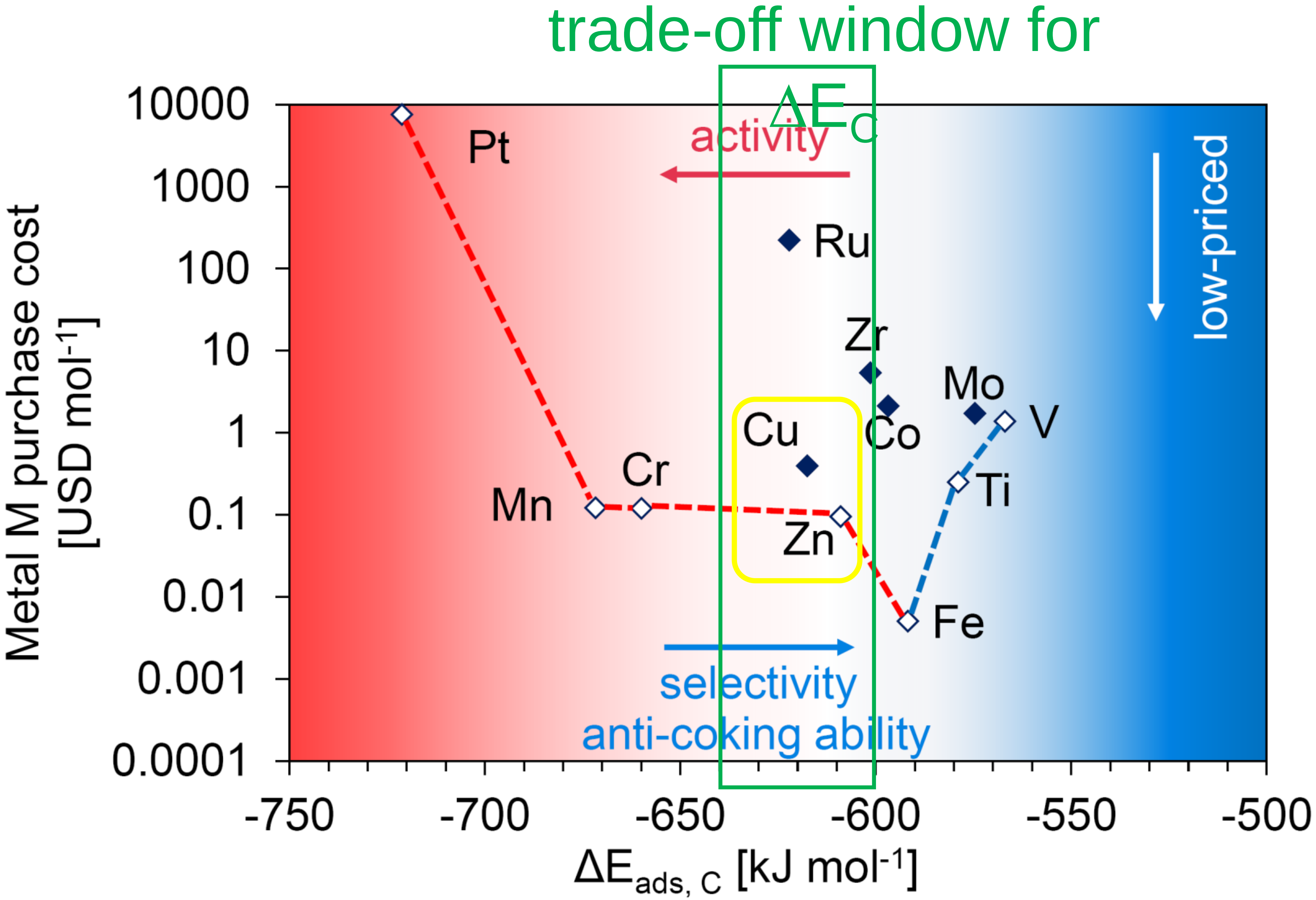


GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

Multi-objective optimization: d-block

–catalyst composition & price



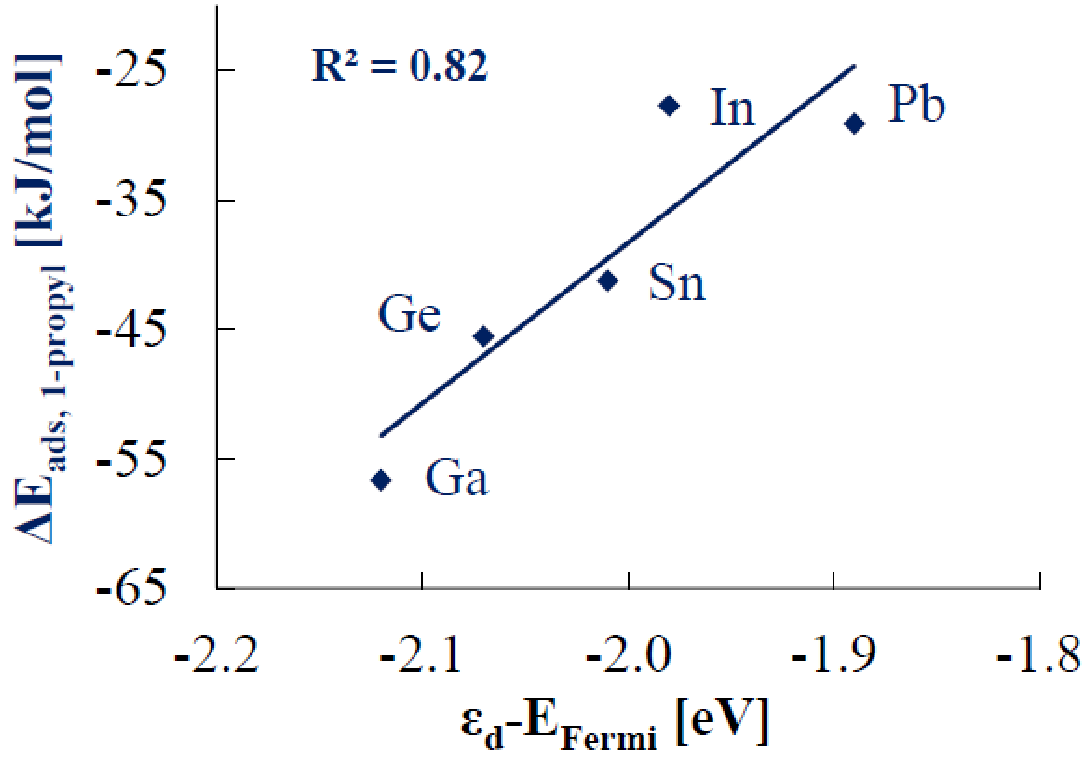
GHENT UNIVERSITY

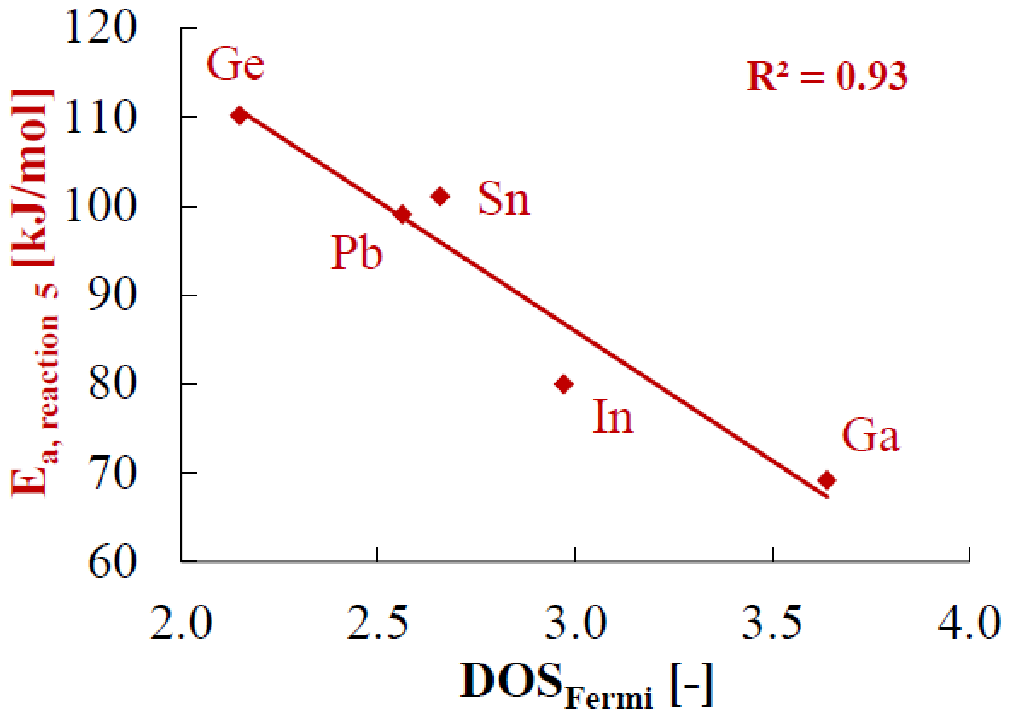
DRIVING CHEMICAL TECHNOLOGY

Identification of catalyst descriptors: p-block

- correlation & regression analysis of DFT data on all important reaction steps
- p-block alloys: two descriptors needed; DOS_{Fermi} and d-band center

$$\Delta E_{r,i}/E_{a,i} = \chi_i + \begin{cases} \zeta_i \cdot DOS_{Fermi} \\ \xi_i \cdot (\varepsilon_d - E_{Fermi}) \end{cases}$$

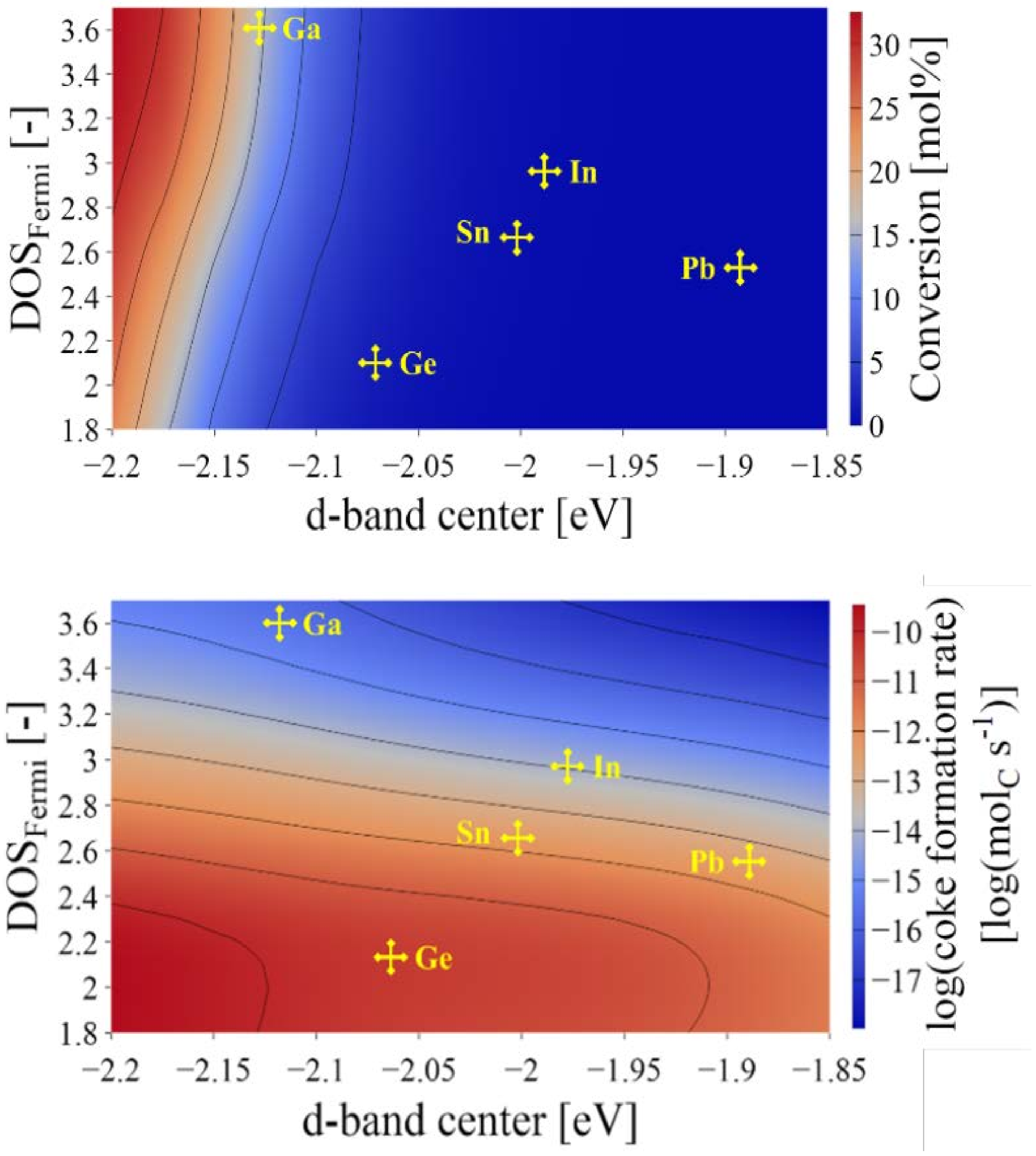




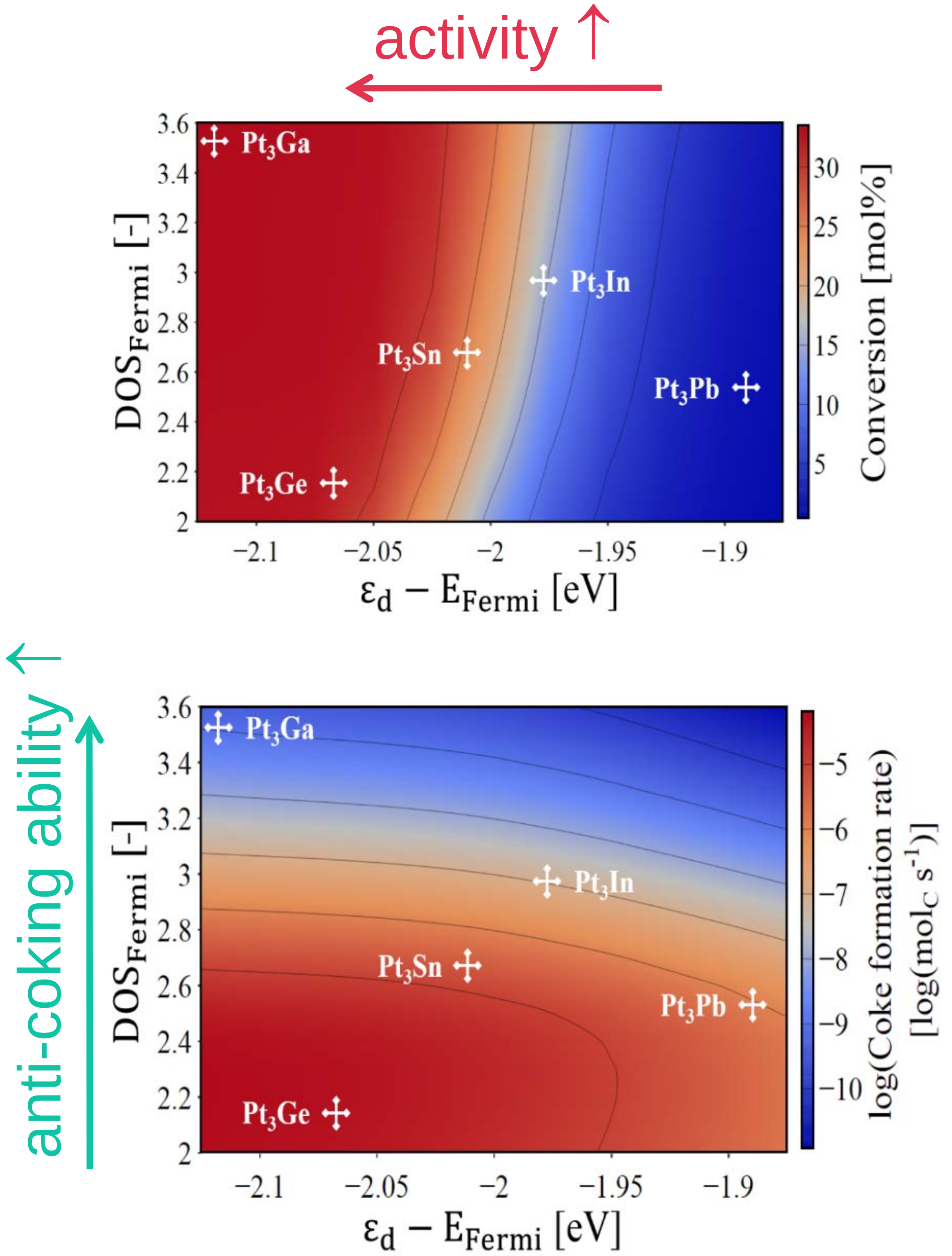
GHENT UNIVERSITY

DRIVING CHEMICAL TECHNOLOGY

μ-kinetic mapping: p-block



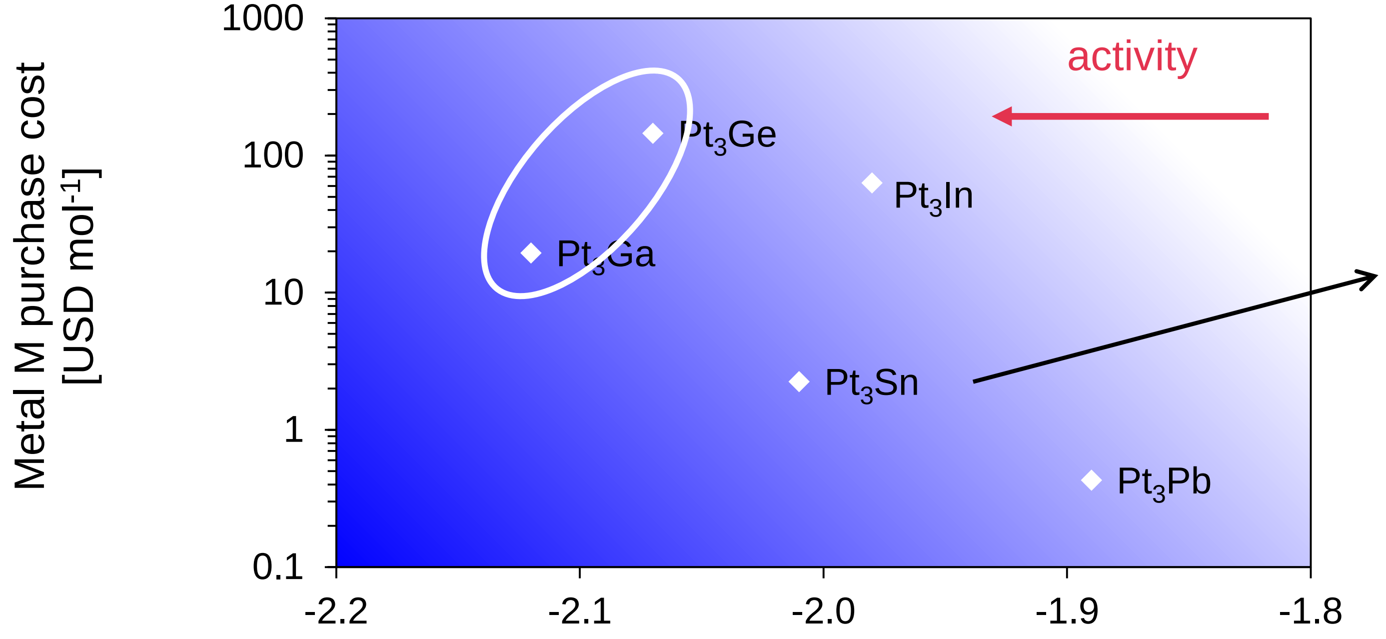
(*T* = 600 °C, *p* = 1 atm, *WHSV* = 882 h^{-1})



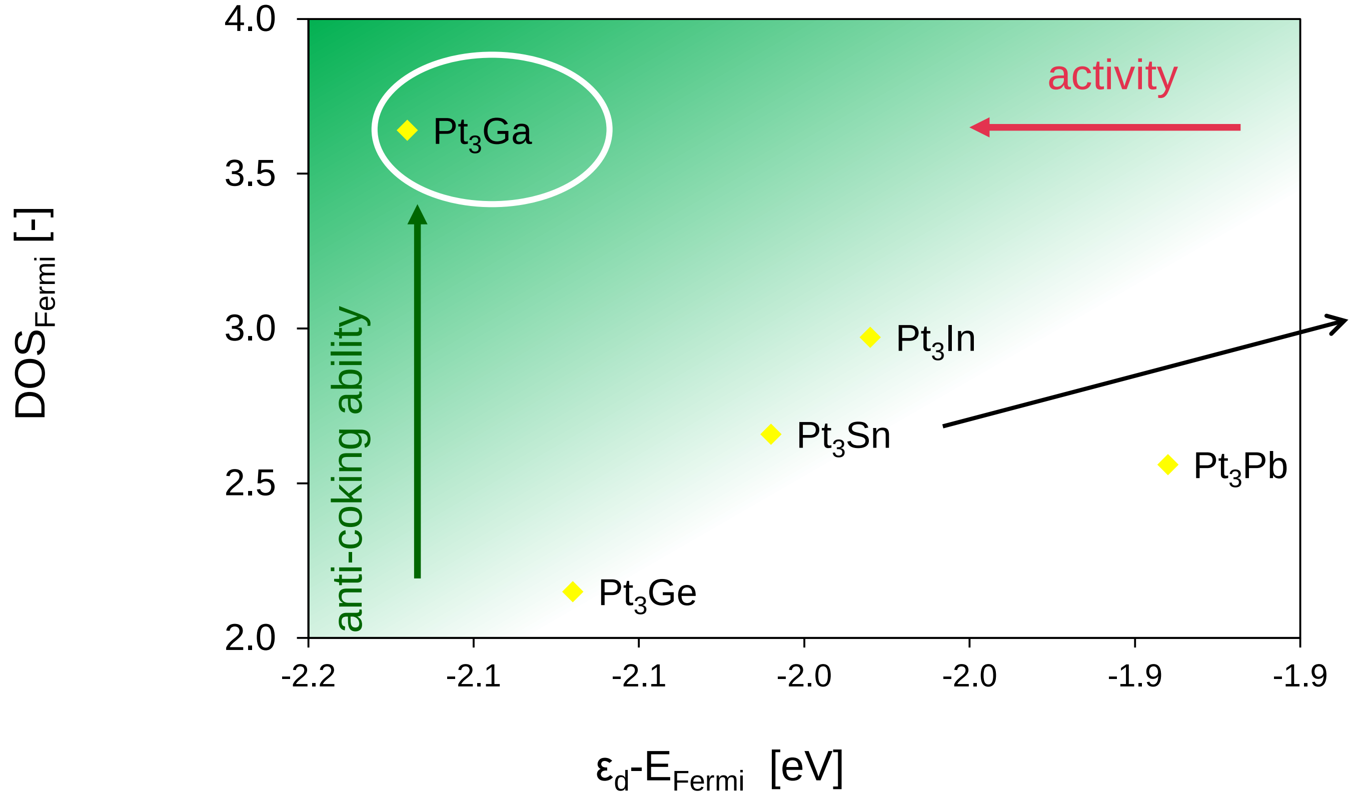
(*T* = 600 °C, *p* = 1 atm, *WHSV* = 8.82 h^{-1})

Multi-objective optimization: p-block

–catalyst composition & price



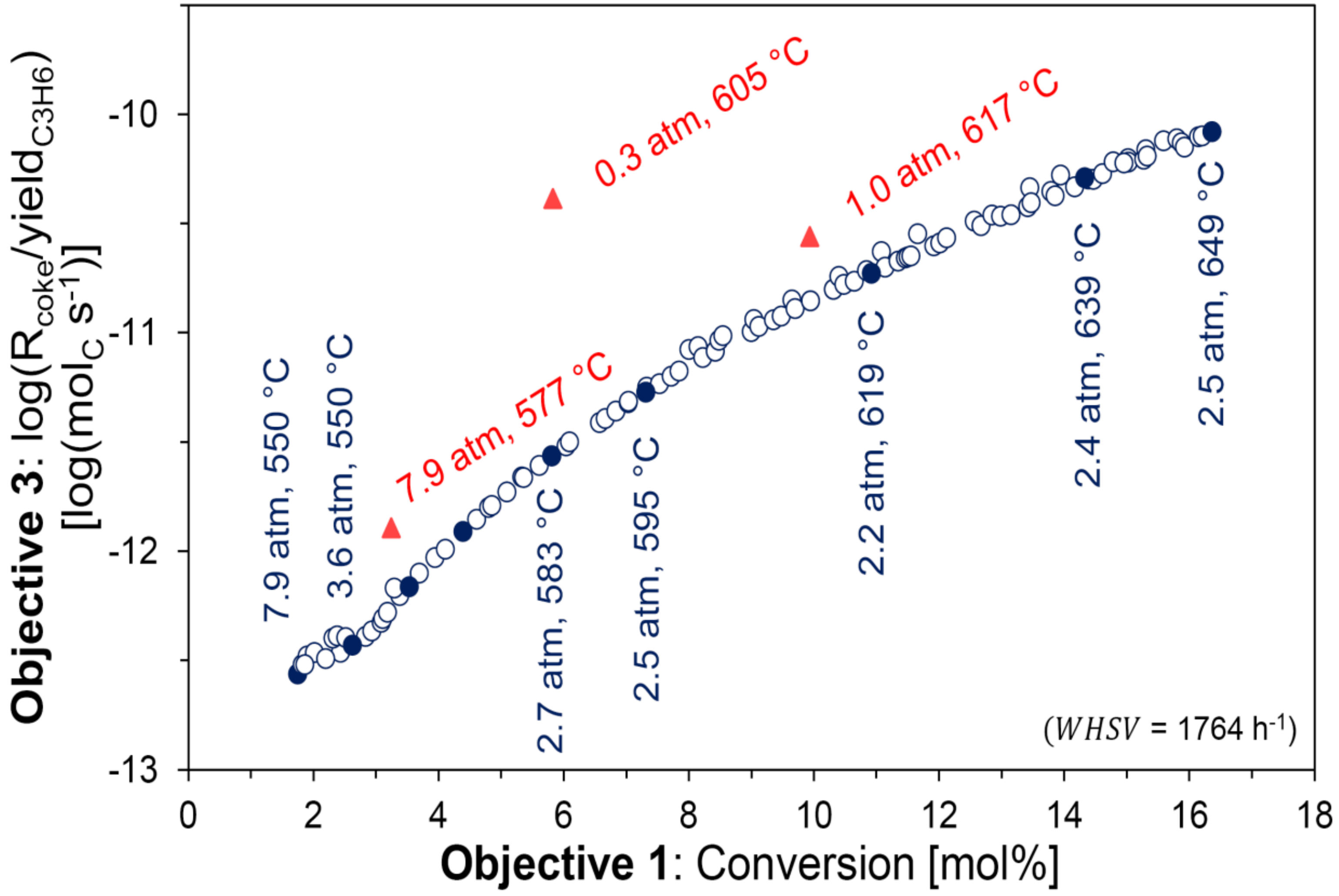
used industrially



used industrially

Multi-objective optimization: p-block

–simultaneous optimization of p and T for Pt_3Ga



- at low single pass conversion

  p > 3 atm

  T < 600°C

- at higher single pass conversion

  p < 3 atm

  T > 600°C

Propane dehydrogenation: take home

Design of bimetallic catalysts can be speeded up by combining:

- first principles based activity-catalyst descriptor relations
- μ-kinetic modelling
- multi-objective optimization

The approach allows defining optimal trade-offs between composition, reaction conditions and catalyst cost allowing to reach predefined ranges of activity, selectivity and coke formation

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

Thank you